Interaction of Metal Ions with Pyrimidine Derivatives: X-ray Crystal Structure of Tetrakis(2-pyrimidinone)copper(II) Perchlorate–Ethanol

By Brian A. Cartwright, Colin D. Reynolds and Andrzej C. Skapski

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

The title complex crystallizes as an ethanol solvate, $[Cu(2\text{-pyrimidinone})_4](ClO_4)_2 \cdot EtOH$, in the orthorhombic space group $Aba2$, with $a = 20 \cdot 022$ (2), $b = 12 \cdot 263$ (1), $c = 11 \cdot 073$ (1) Å, $Z = 4$. Diffractometer data were used to solve the structure, and full-matrix least-squares refinement of 1361 independent reflexions reached $R = 0 \cdot 067$. The Cu atom lies on a diad, and is bonded to an N atom of each ligand to give square planar coordination. The axial positions are effectively blocked by the keto O atoms which are alternately above and below the coordination plane. Independent Cu–N distances are $1 \cdot 992$ and $2 \cdot 004$ Å, with Cu$\cdots$O distances of $2 \cdot 776$ and $2 \cdot 901$ Å. The complex ion has approximate $\overline{4}2m$ (D_{2d}) symmetry. The perchlorate ions and the ethanol molecules are not coordinated, but are involved in hydrogen-bonding.

Introduction

The formation and structure of metal nucleotide complexes is of current interest (*e.g.* Aoki, Clark & Orbell, 1976; Goodgame, Jeeves, Reynolds & Skapski, 1975), and in line with work on metal complexes of nucleotide bases and related compounds the title derivative was prepared (Jeeves, 1976). Electronic spectra and other physical measurements indicated a probable Cu–N square planar coordination with the suggestion of weak interaction along the axial direction (Jeeves, 1976). The nature of the environment about the Cu atom was of interest since the ligand is similar to cytosine. Possible Cu$\cdots$O interaction has been proposed for cytosine complexes as providing some selectivity of Cu binding to such compounds (Sundaralingam & Carrabine, 1971). Additionally, while it was known that the ethanol was firmly held in the crystals it was uncertain whether it was interacting weakly with Cu. Accordingly, a determination of the structure was carried out.

Experimental

Tetrakis(2-pyrimidinone)copper(II) perchlorate was prepared from concentrated cold ethanolic solutions of Cu^{II} perchlorate hexahydrate and 2-pyrimidinone (in a 1:3 molar ratio). Chemical analysis indicated that the purple octahedral crystals contained ethanol of solvation in a Cu:ethanol ratio of 1:1 (Jeeves, 1976).

Photographs showed the crystals to be orthorhombic, with systematic absences *hkl*: $k + l = 2n + 1$, $0kl$: $k = 2n + 1$ and $h0l$: $h = 2n + 1$. These absences are consistent with space groups $Aba2$ and $Acam$; the latter did not give a sensible structure and was discarded. A crystal $0 \cdot 27 \times 0 \cdot 28 \times 0 \cdot 30$ mm was mounted with *c*

parallel to the φ axis on a Siemens off-line four-circle automatic diffractometer, and measurement of high-angle α_1 and α_2 reflexions gave $a = 20 \cdot 022$ (2), $b = 12 \cdot 263$ (1), $c = 11 \cdot 073$ (1) Å, and $U = 2718 \cdot 8$ Å^3. The density based on $Z = 4$, molecular formula $C_{18}H_{22}Cl_2CuN_8O_{13}$ and $M_r = 692 \cdot 9$ is $D_c = 1 \cdot 69$; D_o (by flotation) $= 1 \cdot 67$ g cm^{-3}. $F(000) = 1412$ and μ (Cu $K\alpha$) $= 36 \cdot 9$ cm^{-1}.

Reflexion intensities were measured with Cu $K\alpha$ radiation ($\lambda = 1 \cdot 5418$ Å) at a take-off angle of $3°$, a Ni β-filter, and an Na(Tl)I scintillation counter. The θ–2θ scan technique was employed with a five-value measuring procedure: one side of peak, background, full peak, background on other side of peak, other side of peak (Allen, Rogers & Troughton, 1971). 1361 independent reflexions were measured to $\theta = 70°$, and of these 59 were considered unobserved as their net count was less than $2 \cdot 58\sigma$. The 10,4,0 reflexion was monitored as a reference every 50 reflexions, and its net count did not alter noticeably over the period of data collection (*ca* 4 d). The data were scaled with the reference reflexion, and Lorentz and polarization corrections applied.

Solution and refinement of the structure

A sharpened, origin-removed Patterson synthesis showed the Cu atom to be lying on a twofold axis, and its position was fixed at 0,0,0, to give $R = 0 \cdot 46$. Difference Fourier syntheses and isotropic refinement located the remaining non-hydrogen atoms and R reached $0 \cdot 106$. With only four ethanol molecules per unit cell their position has to involve disorder. A region of electron density about a twofold axis was consistent with this, and in the final refinement a model with a population parameter of $0 \cdot 5$ was used based on likely

hydrogen bonding. In order to get chemically reason-able refinement with such disorder, the ethanol methyl C atom had to be fixed. Refinement of all atoms aniso-tropically (except the ethanol molecule) gave $R = 0.072$, and from the resulting difference map the ring H atoms were located. When these were included as a fixed-atom contribution with the isotropic temperature factors of their parent atoms, R diminished to 0.068. Application of anomalous dispersion correction for both orientations gave identical R values. This suggests that the crystal used may have contained roughly equal pro-portions of regions of opposite polarity, and a slightly bigger reduction in R was obtained with only the real

Table 1. *Atomic coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

The atoms of the 2-pyrimidinone ligands are numbered (mn) where m is the ligand number, and n is the atom number within each ligand.

	x	y	z
Cu(1)	0	0	0
N(11)	−679 (3)	−323 (5)	1265 (6)
C(12)	−590 (3)	−1323 (6)	1786 (8)
N(13)	−1035 (3)	−1578 (5)	2698 (7)
C(14)	−1532 (4)	−916 (7)	3048 (8)
C(15)	−1606 (5)	82 (6)	2525 (9)
C(16)	−1172 (4)	342 (6)	1588 (8)
O(12)	−150 (3)	−1923 (5)	1502 (7)
N(21)	662 (3)	406 (6)	−1280 (6)
C(22)	995 (3)	−510 (6)	−1664 (7)
N(23)	1475 (4)	−389 (7)	−2511 (7)
C(24)	1641 (4)	600 (10)	−2965 (10)
C(25)	1317 (5)	1494 (8)	−2609 (10)
C(26)	846 (4)	1369 (7)	−1745 (9)
O(22)	839 (3)	−1415 (4)	−1236 (7)
Cl(1)	2775 (1)	−2267 (2)	282 (3)
O(1)	2780 (5)	−3439 (7)	112 (12)
O(2)	3407 (5)	−1856 (11)	−76 (13)
O(3)	2651 (4)	−2018 (7)	1537 (9)
O(4)	2275 (10)	−1861 (20)	−442 (16)
O(100)	117 (12)	4319 (21)	1246 (29)
C(101)	126 (10)	4457 (15)	20 (26)
C(102)	124	5692	−307

Table 2. *Fractional coordinates* ($\times 10^3$) *of the H atoms*

The ring hydrogen atoms have the same number as their parent atom, and the methylene hydrogen atoms are H(111) and (121). Calculated positions are in square brackets.

	x	y	z
H(13)	−90	−235	275
H(14)	−185	−130	355
H(15)	−190	80	260
H(16)	−120	107	121
H(23)	180	−100	−264
H(24)	196	85	−354
H(25)	137	221	−285
H(26)	67	219	−167
[H(111)	51	410	−388]
[H(121)	−29	410	−388]

parts of the correction. Introduction of a weighting scheme did not affect R but improved the standard deviations up to 50%. The final R was 0.067, and the positions of the non-hydrogen atoms are given in Table 1.† Table 2 lists the positions of those H atoms which were located, or those which could be calculated.

Scattering factors of Cromer & Waber (1965), and for H of Stewart, Davidson & Simpson (1965), were used, with the anomalous dispersion corrections for Cu and Cl of Cromer & Liberman (1970). The weighting scheme was of the type suggested by Hughes (1941), where $w = 1$ for $F < F^*, \sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 17$. In the final stages of refinement the July 1974 update of X-RAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used. Most of the cal-culations were performed on the University of London CDC 7600 computer, while steering-tape generation, data processing and structural illustrations were done on the Imperial College CDC 6400 machine.

Description of the structure and discussion

The crystal structure consists of three discrete com-ponents: tetrakis(2-pyrimidinone)copper(II) cations, perchlorate anions, and ethanol molecules of solvation. Table 3 gives the more important interatomic distances and bond angles, while Fig. 1 shows the complex cation together with the thermal vibration ellipsoids of the non-hydrogen atoms (Johnson, 1965).

The cation has crystallographic twofold symmetry, and the Cu atom is bonded to a ring N on each of the 2-pyrimidinone ligands. A square planar coordination is found with N—Cu—N *cis* angles in the range 89.8 to 90.6°. The two independent Cu—N distances are 1.992 and 2.004 Å, which are unexceptional. The exocyclic O atoms are alternately above and below the coordination plane, with Cu···O distances of 2.776 and 2.901 Å.
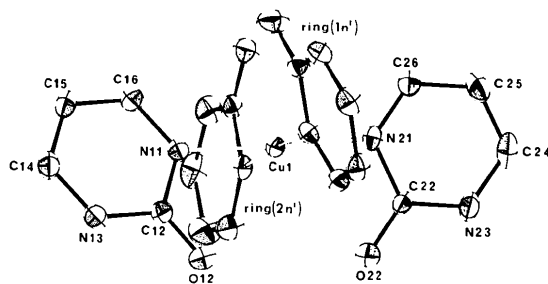
Fig. 1. Structure of the [Cu(2-pyrimidinone)$_4$]$^{2+}$ ion. Thermal vi-bration ellipsoids are scaled to include 30% probability.

Table 3. *Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses*

Superscripts refer to atoms in the following positions:

(i) $-x, -y, z$; (ii) $\frac{1}{2} - x, y, z - \frac{1}{2}$; (iii) $-x, -\frac{1}{2} - y, \frac{1}{2} + z$.

(a) Complex cation

Cu(1)–N(11)	1·992 (6)	Cu(1)–N(21)	2·004 (6)
Cu(1)···O(12)	2·901 (7)	Cu(1)···O(22)	2·776 (6)
N(11)–C(12)	1·368 (10)	N(21)–C(22)	1·374 (10)
C(12)–N(13)	1·382 (10)	C(22)–N(23)	1·350 (11)
N(13)–C(14)	1·341 (11)	N(23)–C(24)	1·354 (14)
C(14)–C(15)	1·362 (12)	C(24)–C(25)	1·333 (15)
C(15)–C(16)	1·392 (13)	C(25)–C(26)	1·393 (14)
C(16)–N(11)	1·328 (10)	C(26)–N(21)	1·325 (11)
C(12)–O(12)	1·190 (9)	C(22)–O(22)	1·247 (9)
N(11)–Cu(1)–N(11ⁱ)	90·6 (3)	N(11)–Cu(1)–N(21ⁱ)	89·8 (3)
N(21)–Cu(1)–N(21ⁱ)	90·0 (3)	N(21)–Cu(1)–N(11ⁱ)	89·8 (3)
N(11)–Cu(1)–N(21)	176·9 (3)		
N(11)–Cu(1)–O(12)	50·6 (2)	N(21)–Cu(1)–O(22)	53·6 (2)
Cu(1)–N(11)–C(12)	112·7 (5)	Cu(1)–N(21)–C(22)	109·7 (5)
N(11)–C(12)–O(12)	122·7 (7)	N(21)–C(22)–O(22)	119·3 (7)
C(12)–O(12)–Cu(1)	74·1 (5)	C(22)–O(22)–Cu(1)	77·4 (4)
Cu(1)–N(11)–C(16)	125·0 (5)	Cu(1)–N(21)–C(26)	130·6 (6)
C(16)–N(11)–C(12)	122·3 (7)	C(26)–N(21)–C(22)	119·7 (7)
N(11)–C(12)–N(13)	115·2 (6)	N(21)–C(22)–N(23)	118·0 (7)
N(13)–C(12)–O(12)	122·1 (7)	N(23)–C(22)–O(22)	122·7 (7)
C(12)–N(13)–C(14)	123·6 (7)	C(22)–N(23)–C(24)	122·1 (8)
N(13)–C(14)–C(15)	120·2 (8)	N(23)–C(24)–C(25)	120·4 (9)
C(14)–C(15)–C(16)	117·0 (8)	C(24)–C(25)–C(26)	117·6 (9)
C(15)–C(16)–N(11)	121·6 (7)	C(25)–C(26)–N(21)	122·1 (8)

(b) Perchlorate anion

Cl(1)–O(1)	1·450 (9)	Cl(1)–O(2)	1·418 (12)
Cl(1)–O(3)	1·444 (10)	Cl(1)–O(4)	1·375 (20)
O(1)–Cl(1)–O(2)	108·1 (7)	O(2)–Cl(1)–O(3)	110·3 (7)
O(1)–Cl(1)–O(3)	109·6 (6)	O(2)–Cl(1)–O(4)	110·9 (1·0)
O(1)–Cl(1)–O(4)	106·8 (1·1)	O(3)–Cl(1)–O(4)	111·0 (9)

(c) Ethanol solvate molecule

O(100)–C(101)	1·37 (4)	O(100)–C(101)–C(102)	110·5
C(101)–C(102)	1·56		

(d) Hydrogen bonds

N(23)···O(3ⁱⁱ)	2·859 (11)	N(23)–H(23)–O(3ⁱⁱ)	160
N(13)···O(22ⁱⁱⁱ)	2·758 (9)	N(13)–H(13)–O(22ⁱⁱⁱ)	145
O(100)···O(12)	2·95 (3)		

They are positioned so as to block the axial coordination sites. The ion has approximate $\bar{4}2m$ (D_{2d}) point symmetry.

Within the pyrimidine rings the bond lengths and angles are in good agreement with the corresponding values found in uncoordinated 2-pyrimidinone (Furberg & Solbakk, 1970) and in Cu(cytosine)$_2$Cl$_2$ (Sundaralingam & Carrabine, 1971). The slight differences between the two independent rings are probably not significant.

It can be seen from Fig. 2 that the ligand rings are approximately normal to the coordination plane. Thus ring (1n) makes an angle of 79° with this plane, while for ring (2n) this angle is 85°. The *trans* rings deviate from the normal in opposite directions, thus the angle between rings (1n) and (2n) is 17°. Results of least-

squares calculations listed in Table 4 show that the rings are satisfactorily planar and that the keto O atoms deviate from these planes by at most 0·02 Å, which is not statistically significant. In each case the Cu atom lies reasonably close to the planes of the rings, with a maximum deviation of 0·07 Å. The coordination plane is slightly distorted towards tetrahedral, with the N atoms ±0·054 Å from the plane. With each ligand the bonded N lies on the opposite side of the plane to the keto O atom.

Apart from electrostatic attraction, the other main cohesive force is hydrogen-bonding. Three types of hydrogen bonds are present: O(22)···N(13), which connect rings from different cations into an infinite two-dimensional network; O(12)···O(100), which help to tie down the solvated ethanol molecules; and

Table 4. *Planarity of the coordination plane and the 2-pyrimidinone rings*

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space, and distances of atoms from the least-squares planes are in Å.

$$-6·32x + 11·63y = 0$$

Cu(1)	0·000	N(11)	0·054	N(11ⁱ)	−0·054
N(21)	0·054	N(21ⁱ)	−0·054		

Not defining plane: O(12) −2·143, O(22) −2·177, O(12ⁱ) 2·143, O(22ⁱ) 2·177

$$12·26x + 5·09y + 7·45z = −0·06$$

N(11)	0·009	C(12)	−0·001	N(13)	0·002
C(14)	−0·010	C(15)	0·017	C(16)	−0·017

Not defining plane: O(12) 0·020, Cu(1) 0·064

$$13·54x + 1·59y + 8·03z = −0·07$$

N(21)	0·005	C(22)	0·002	N(23)	−0·009
C(24)	0·009	C(25)	−0·002	C(26)	−0·005

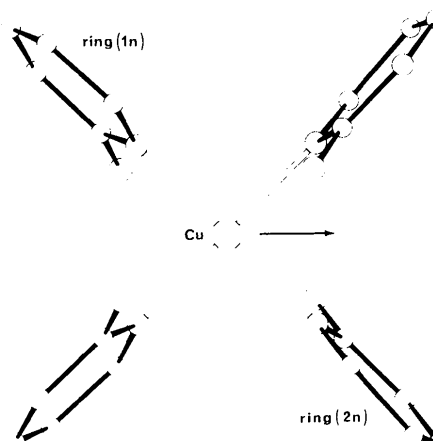Not defining plane: O(22) −0·011, Cu(1) 0·071

Fig. 2. The complex cation viewed normal to the copper coordination plane and to the crystallographic twofold axis.

N(23)···O(3), which connect the cations and the perchlorate ions. These last two hydrogen bonds do not form extended networks. Fig. 3 shows the packing (Johnson, 1965).

The perchlorate ion shows the commonly observed tendency to slight disorder/high thermal vibration. The thermal parameters of its O atoms are consistent with a situation in which this ion is firmly anchored by the hydrogen bond to O(3) and has a degree of latitude for the other three O atom positions.

The pyrimidinone O(12) and O(22) are 2·901 and 2·776 Å respectively from the Cu atom, and in this position the O atoms, particularly O(22), may have some slight direct interaction with the metal. Some workers have invoked the concept of semi-coordination (e.g. Hathaway & Billing, 1970) to account for the fairly high number of similar compounds with off-axis

Cu···O distances of around 2·8 Å. Such distances are often found in cytosine–Cu complexes, and a comparison of relevant distances and angles is made in Table 5.

In the title complex we have two Cu···O distances to consider. Cu(1)···O(12), 2·901 Å, is related to an O(12)–C(12) length of 1·190 Å, a Cu(1)–O(12)–C(12) angle of 74·1° and a Cu(1)–N(11)–C(12) angle of 112·6°. Cu(1)···O(22), 2·776 Å, is related to a longer O(22)–C(22) length of 1·247 Å, a larger Cu(1)–O(22)–C(22) angle of 77·4° and a smaller Cu(1)–N(21)–C(22) angle of 109·7°. Both Cu–N(m1)–C(m2) angles are less than the 117° usually found in covalent N-substituted pyrimidines (Voet & Rich, 1970). Nevertheless, this evidence for a positive Cu···O interaction is complicated by the presence of hydrogen bonding. Thus the significantly
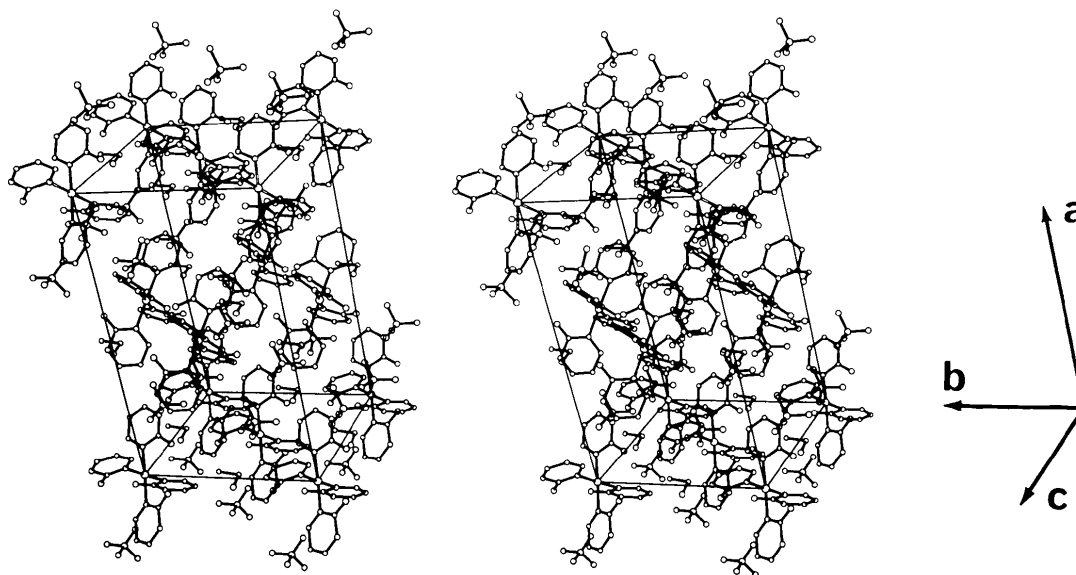

Fig. 3. A stereoscopic view of the crystal structure. For clarity only one ethanol orientation is shown.

Table 5. *A comparison of the geometries of possible* Cu···O *interactions in some related complexes*

Compound	Cu···O(2) (Å)	Cu···C(2) (Å)	Cu–O(2)–C(2) (°)	Cu–N (Å)	
[Cu(2-pyrimidinone)₄]²⁺	2·78, 2·90	2·79, 2·82	77, 74	2·00, 1·99	This work
CuCl₂(cytosine)₂	2·74, 2·88	2·71, 2·81	76, 75	1·97, 1·95	Sundaralingam & Carrabine (1971)
[Cu(N-salicylidene-N¹-methylenediamine)(cytosine)]⁺	2·77	2·76	77	2·01	Szalda, Marzili & Kistenmacher (1975b)
Cu(glycylglycinato)(cytosine)	2·82	2·78	76	1·98	Kistenmacher, Szalda & Marzili (1975)
	2·81	—	—	1·97	Saito, Terashima, Sakai, & Tomita (1974)
Cu(glycylglycinato)(cytidine)	2·68, 2·80	2·73, 2·76	78, 76	2·04, 1·97	Szalda, Marzili & Kistenmacher (1975a)

longer C—O distance is associated with an apparently stronger hydrogen bond formed by O(22) compared with O(12). Similarly the angles at the donor N atoms may be sensitive to the constraints imposed by hydrogen bonds formed by both N(m3) and O(m2). However, the fact that a strong O(22) hydrogen bond is associated with the shorter Cu $\cdots$ O distance is consistent with some Cu $\cdots$ O interaction.

References

ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* B27, 1325–1337.

AOKI, K., CLARK, G. R. & ORBELL, J. D. (1976). *Biochim. Biophys. Acta*, 425, 369–371.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.

FURBERG, S. & SOLBAKK, J. (1970). *Acta Chem. Scand.* 24, 3230–3236.

GOODGAME, D. M. L., JEEVES, I., REYNOLDS, C. D. & SKAPSKI, A. C. (1975). *Biochem. J.* 151, 467–468.

HATHAWAY, B. J. & BILLING, D. E. (1970). *Coord. Chem. Rev.* 5, 143–207.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* 63, 1737–1752.

JEEVES, I. (1976). PhD Thesis, London.

JOHNSON, C. K. (1965). *ORTEP*, Oak Ridge National Laboratory Report ORNL-3794.

KISTENMACHER, T. J., SZALDA, D. J. & MARZILI, L. G. (1975). *Acta Cryst.* B31, 2416–2422.

SAITO, K., TERASHIMA, R., SAKAI, T. & TOMITA, K. (1974). *Biochem. Biophys. Res. Commun.* 61, 83–86.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). Univ. of Maryland Tech. Rep. TR-192.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

SUNDARALINGAM, M. & CARRABINE, J. A. (1971). *J. Mol. Biol.* 61, 287–309.

SZALDA, D. J., MARZILI, L. G. & KISTENMACHER, T. J. (1975a). *Biochem. Biophys. Res. Commun.* 63, 601–605.

SZALDA, D. J., MARZILI, L. G. & KISTENMACHER, T. J. (1975b). *Inorg. Chem.* 14, 2076–2081.

VOET, D. & RICH, A. (1970). *Progr. Nucleic Acid Res.* 10, 183–265.

Kristall- und Molekülstruktur von Tetracyclohexylbiphosphin

VON R. RICHTER, J. KAISER UND J. SIELER

Sektion Chemie der Karl-Marx-Universität, 701 Leipzig, Deutsche Demokratische Republik

UND H. HARTUNG UND C. PETER

Sektion Chemie der Martin-Luther-Universität, 402 Halle, Deutsche Demokratische Republik

The crystal structure of tetracyclohexylbiphosphine $(C_6H_{11})_2P—P(C_6H_{11})_2$ has been determined by three-dimensional X-ray analysis with film data. The crystals are triclinic, space group $P\bar{1}$ with two molecules in a cell of dimensions $a = 12.72$ (1), $b = 10.98$ (1), $c = 11.01$ (1) Å, $\alpha = 110.9$ (1), $\beta = 114.7$ (1), $\gamma = 102.0$ (1)°. The structure has been solved by Patterson and Fourier syntheses and refined by the block-diagonal least-squares method on 2731 independent reflexions. H atoms could not be located in a difference electron density map, but were included in the calculation assuming tetrahedral positions and C—H distances of 1.00 Å. The final R index including the unobserved reflexions is $R = 0.117$. The bond distances are P—P = 2.215 (3), P—C (average) = 1.883 (4), C—C (average) = 1.538 (3) Å. The cyclohexyl rings have the chair conformation with P occupying equatorial positions. The conformation of the molecule in the solid state is approximately semi-eclipsed.

Einleitung

Tetraorganobiphosphine, $R_2P—PR_2$, sind in der präparativen und Strukturchemie des Phosphors seit einiger Zeit von grösserem Interesse. Diese Verbindungen zeichnen sich u.a. durch ein ausgeprägtes Reaktionsvermögen gegenüber Übergangsmetallhalogeniden und -carbonylen aus. Während an den entsprechenden