

## Structure of a Benzene Solvate of $\alpha$ -Furildioxime

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### Abstract

The unit-cell parameters for a benzene solvate of  $\alpha$ -furildioxime,  $C_{10}H_8N_2O_4 \cdot \frac{1}{4}C_6H_6$ , are  $a = 12.426$  (4),  $b = 22.583$  (6),  $c = 8.208$  (2) Å and  $\beta = 90.10$  (2)°; space group  $P2_1/c$ ,  $d_c = 1.382$  Mg m<sup>-3</sup>,  $Z = 8$ . Least-squares refinement of the two furildioxime and  $\frac{1}{4}$  benzene molecules in the asymmetric unit against 2032 reflections gave a final  $R$  of 0.058. The red crystals used for the structure determination resulted from an attempted synthesis of a Re–furildioxime complex, but no Re was found in the crystal structure. Both furildioxime molecules are in the  $\alpha$  conformation, which allowed for a detailed comparison of the bond lengths, bond angles and torsion angles in each.

### Introduction

Due to the importance and wide applicability of <sup>99m</sup>Tc as a diagnostic tool in radiology (Subramanian, Rhodes, Cooper & Sodd, 1975), our goal in this work was the synthesis of clathrochelates of Tc. Preliminary work has been carried out with Re because it is chemically similar to Tc and has no radiation hazard. Fergusson & Gainsford (1964) reported that a tris-furildioxime Re complex could be formed starting with furildioxime and  $K_2ReCl_6$ . In the light of this work and Boston's approach to making clathrochelates from tris-dioxime complexes and capping agents (Boston & Rose, 1968, 1973; Jackels, Zektzer & Rose, 1977), we attempted a similar synthesis of the tris-furildioxime Re complex. Red crystals resulted from a synthesis employing  $K_2ReCl_6$ , furildioxime and aqueous ammonia. These crystals were found suitable for the single-crystal X-ray diffraction study described in this paper. The crystals do not contain amounts of Re detectable in the X-ray experiment and consist simply of molecules of  $\alpha$ -furildioxime and benzene.

### Experimental and structure solution

A sample of  $K_2ReCl_6$  [0.49 g (1.0 mmol)] was dissolved in 30 ml H<sub>2</sub>O and stirred for 30 min under N<sub>2</sub>. 0.76 g (3.5 mmol) of commercially available (G. F. Smith) furildioxime\* dissolved in 4 ml acetone was added to the  $K_2ReCl_6$  solution with stirring with no color change, then 0.68 ml 28% aqueous ammonia solution was added to the  $ReCl_6^{2-}$ –furildioxime system over a 45 min period. The solution changed to a reddish color on addition of the first drop of the ammonia solution, became more violet as the addition continued, and finally deposited a violet solid. After stirring overnight under N<sub>2</sub>, the solution was filtered in the air and the violet solid collected. Ether was added to the solid, causing much of it to dissolve and giving a red-violet solution. The solution was filtered and a small amount of it was placed in a flask with two drops of water, to which benzene was then added. The solution was slowly evaporated, yielding a very few small red crystals, one of which was used in the X-ray study.

Three-dimensional diffraction data were collected from a crystal of approximate dimensions 0.2 × 0.6 × 0.06 mm using a computer-controlled four-circle diffractometer ( $\lambda = 0.71069$  Å,  $\omega$ – $2\theta$  scans, scan rate 2° min<sup>-1</sup> in  $2\theta$ , 20 s backgrounds on either side of the reflection, nine standard reflections). The systematic absences ( $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ) indicated the space group  $P2_1/c$ . A complete data set was collected to a  $2\theta$  value of 45°. Due to the large proportion of weak reflections in the range  $45^\circ < 2\theta < 50^\circ$ , this shell of data was not completed. The standard reflections indicated radiation damage of less than 1%. No absorption correction was applied since measurements of a reflection at  $\chi = 90^\circ$  as a function of  $\phi$  did not indicate the need for one. The linear absorption

\* Typical analyses of commercial samples of furildioxime show that they consist of approximately 50%  $\alpha$  and 50%  $\gamma$  isomers (see Fryer, Galliford & Yardley, 1963).

coefficient for the correct unit-cell contents is  $0.12 \text{ mm}^{-1}$ .

Analysis of the Patterson map suggested a possible site for a Re atom, but this failed to lead to development of a satisfactory model. *MULTAN* was then applied in an automated mode and yielded a set of connected atoms recognized as a furildioxime molecule. This provided the initial phases, and an additional part of the structure, a second furildioxime molecule in the asymmetric unit, was obtained by inspection of electron density maps after least-squares refinement of the first molecule. At an  $R$  ( $= \sum |F_o| - |F_c| / \sum |F_o|$ ) of 0.236, the remaining density in a  $\Delta F$  map was identified as a benzene molecule at the center of symmetry, thus ruling out the presence of Re in the crystal. When *MULTAN* was re-run, using normalized structure factors calculated for the actual cell contents, connected atoms corresponding to both furildioxime molecules were found in the  $E$  map.

All the H atoms in the structure were evident in a  $\Delta F$  map. Positional and isotropic thermal parameters for the H atoms were refined in one least-squares cycle keeping the other atoms fixed. The final refinement stages were blocked least-squares cycles of the non-hydrogen atoms only, minimizing the function  $\sum w|F_o - |F_c||^2$  with weights of  $1/\sigma^2(F)$ . The scattering factors used for the C, N and O atoms were those of Cromer & Mann (1968), and that of Stewart, Davidson & Simpson (1965) was used for H. The final  $R$  is 0.058 for 2032 reflections with  $F_o > 4\sigma(F_o)$  out of a total data set of 3049 reflections. The goodness of fit is 1.658 and the weighted  $R$  is 0.059.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36456 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

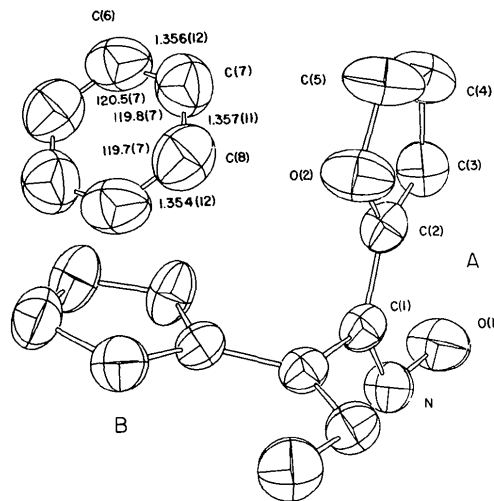


Fig. 1. Thermal ellipsoids and the labeling scheme for the non-hydrogen atoms, and bond lengths (Å) and angles ( $^\circ$ ) for the benzene ring.

Table 1. Atomic parameters

(a) Coordinates ( $\times 10^4$ ) and  $U_{eq}$  ( $\times 10^3$ ) for the non-hydrogen atoms. [ $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ ;  $\sigma(U_{eq})$  0.003; labels A and B are two halves of one molecule, while C and D are two halves of the other molecule.]

| Half molecule |   | x          | y         | z         | $U_{eq}$ ( $\text{\AA}^2$ ) |
|---------------|---|------------|-----------|-----------|-----------------------------|
| C(1)          | A | -4283 (3)  | -1125 (2) | 1069 (5)  | 44                          |
| C(2)          | A | -3259 (3)  | -1379 (2) | 644 (5)   | 48                          |
| C(3)          | A | -2337 (3)  | -1199 (2) | -110 (5)  | 64                          |
| C(4)          | A | -1644 (4)  | -1705 (2) | -127 (6)  | 80                          |
| C(5)          | A | -2166 (4)  | -2143 (2) | 586 (7)   | 89                          |
| N             | A | -4626 (2)  | -614 (1)  | 634 (4)   | 53                          |
| O(1)          | A | -3876 (2)  | -311 (1)  | -342 (4)  | 78                          |
| O(2)          | A | -3162 (2)  | -1966 (1) | 1082 (4)  | 73                          |
| C(1)          | B | -5041 (3)  | -1480 (2) | 2085 (5)  | 42                          |
| C(2)          | B | -4794 (3)  | -1591 (2) | 3774 (5)  | 44                          |
| C(3)          | B | -5225 (3)  | -1913 (2) | 4988 (6)  | 56                          |
| C(4)          | B | -4598 (4)  | -1823 (2) | 6398 (5)  | 64                          |
| C(5)          | B | -3821 (4)  | -1448 (2) | 5969 (5)  | 70                          |
| N             | B | -5866 (2)  | -1685 (1) | 1309 (4)  | 49                          |
| O(1)          | B | -6531 (2)  | -2039 (1) | 2284 (4)  | 63                          |
| O(2)          | B | -3909 (2)  | -1296 (1) | 4354 (3)  | 62                          |
| C(1)          | C | -8483 (3)  | -3192 (2) | 666 (5)   | 49                          |
| C(2)          | C | -9534 (3)  | -3412 (2) | 229 (5)   | 54                          |
| C(3)          | C | -10331 (3) | -3249 (2) | -789 (6)  | 68                          |
| C(4)          | C | -11135 (4) | -3683 (3) | -655 (7)  | 82                          |
| C(5)          | C | -10804 (4) | -4078 (2) | 400 (8)   | 91                          |
| N             | C | -8083 (2)  | -2669 (1) | 371 (4)   | 57                          |
| O(1)          | C | -8810 (2)  | -2309 (1) | -446 (4)  | 73                          |
| O(2)          | C | -9802 (2)  | -3932 (1) | 989 (4)   | 77                          |
| C(1)          | D | -7704 (3)  | -3604 (2) | 1487 (5)  | 49                          |
| C(2)          | D | -7297 (3)  | -4107 (2) | 566 (5)   | 53                          |
| C(3)          | D | -6592 (4)  | -4566 (2) | 842 (7)   | 75                          |
| C(4)          | D | -6512 (4)  | -4866 (2) | -653 (7)  | 79                          |
| C(5)          | D | -7148 (4)  | -4604 (2) | -1720 (6) | 77                          |
| N             | D | -7441 (3)  | -3459 (1) | 2947 (4)  | 57                          |
| O(1)          | D | -6685 (2)  | -3850 (1) | 3613 (4)  | 73                          |
| O(2)          | D | -7650 (2)  | -4130 (1) | -1013 (4) | 68                          |

Benzene molecule

|      |          |          |           |     |
|------|----------|----------|-----------|-----|
| C(6) | -806 (5) | 392 (3)  | 243 (12)  | 108 |
| C(7) | -590 (6) | -25 (4)  | 1388 (8)  | 108 |
| C(8) | 220 (7)  | -418 (3) | 1144 (10) | 110 |

(b) Coordinates ( $\times 10^3$ ) and isotropic  $U$  values ( $\times 10^2$ ) for the hydrogen atoms

|        | x         | y        | z        | $U$ ( $\text{\AA}^2$ ) |
|--------|-----------|----------|----------|------------------------|
| H(C3A) | -216 (3)  | -81 (2)  | -67 (5)  | 10 (1)                 |
| H(C4A) | -89 (3)   | -171 (2) | -72 (5)  | 11 (1)                 |
| H(C5A) | -201 (3)  | -262 (2) | 87 (5)   | 12 (1)                 |
| H(O1A) | -429 (3)  | 4 (2)    | -82 (5)  | 14 (1)                 |
| H(C3B) | -588 (3)  | -213 (2) | 490 (5)  | 9 (1)                  |
| H(C4B) | -460 (3)  | -202 (2) | 756 (5)  | 10 (1)                 |
| H(C5B) | -314 (3)  | -129 (2) | 652 (5)  | 11 (1)                 |
| H(O1B) | -714 (3)  | -225 (2) | 148 (5)  | 12 (1)                 |
| H(C3C) | -1034 (3) | -289 (2) | -164 (5) | 10 (1)                 |
| H(C4C) | -1183 (3) | -368 (2) | -132 (5) | 11 (1)                 |
| H(C5C) | -1099 (3) | -443 (2) | 71 (5)   | 10 (1)                 |
| H(O1C) | -816 (3)  | -199 (2) | -111 (5) | 12 (1)                 |
| H(C3D) | -621 (3)  | -452 (2) | 182 (5)  | 12 (1)                 |
| H(C4D) | -608 (3)  | -520 (2) | -91 (5)  | 11 (1)                 |
| H(C5D) | -745 (3)  | -467 (2) | -287 (5) | 12 (1)                 |
| H(O1D) | -617 (3)  | -365 (2) | 467 (5)  | 10 (1)                 |
| H(C6)  | -137 (5)  | 63 (3)   | 40 (8)   | 22 (3)                 |
| H(C7)  | -112 (5)  | -11 (2)  | 230 (8)  | 20 (3)                 |
| H(C8)  | 32 (5)    | -76 (3)  | 185 (8)  | 20 (3)                 |

Table 2. Bond lengths (Å), bond angles (°) and torsion angles (°) for the furildioxime molecules

Primed atoms refer to the other half of the same molecule.

|                       | Half molecule |            |            |            | Average value<br>and e.s.d. from the<br>four independent<br>measurements |
|-----------------------|---------------|------------|------------|------------|--|
|                       | A             | B          | C          | D          |  |
| C(1)'-C(1)            | 1.493 (6)     |            | 1.502 (5)  |            | 1.497  |
| C(1)-N                | 1.281 (5)     | 1.292 (5)  | 1.304 (5)  | 1.284 (5)  | 1.290 (10)   |
| N-O(1)                | 1.408 (4)     | 1.402 (4)  | 1.387 (4)  | 1.400 (4)  | 1.399 (9)  |
| C(1)-C(2)             | 1.439 (6)     | 1.441 (6)  | 1.442 (6)  | 1.456 (6)  | 1.444 (8)  |
| C(2)-C(3)             | 1.365 (6)     | 1.346 (6)  | 1.346 (6)  | 1.376 (6)  | 1.358 (15)   |
| C(3)-C(4)             | 1.431 (6)     | 1.409 (6)  | 1.404 (7)  | 1.405 (8)  | 1.412 (13)   |
| C(4)-C(5)             | 1.320 (7)     | 1.332 (7)  | 1.309 (8)  | 1.319 (7)  | 1.320 (9)  |
| C(5)-O(2)             | 1.363 (6)     | 1.374 (5)  | 1.375 (6)  | 1.369 (5)  | 1.370 (5)  |
| O(2)-C(2)             | 1.379 (5)     | 1.370 (5)  | 1.371 (5)  | 1.369 (5)  | 1.372 (5)  |
| C(1)'-C(1)-N          | 115.4 (3)     | 114.7 (4)  | 113.5 (3)  | 115.1 (4)  | 114.7 (8)  |
| C(1)-N-O(1)           | 112.1 (3)     | 113.0 (3)  | 111.9 (3)  | 111.9 (3)  | 112.2 (5)  |
| C(1)'-C(1)-C(2)       | 118.7 (4)     | 119.8 (3)  | 118.8 (4)  | 118.3 (4)  | 118.9 (6)  |
| N-C(1)-C(2)           | 125.8 (4)     | 125.4 (4)  | 127.7 (4)  | 126.6 (4)  | 126.4 (10)   |
| C(1)-C(2)-C(3)        | 137.2 (4)     | 136.2 (4)  | 136.5 (4)  | 136.4 (4)  | 136.6 (4)  |
| C(2)-C(3)-C(4)        | 105.8 (4)     | 108.1 (4)  | 106.5 (4)  | 105.4 (4)  | 106.5 (12)   |
| C(3)-C(4)-C(5)        | 107.3 (4)     | 105.9 (4)  | 107.7 (5)  | 108.7 (4)  | 107.4 (12)   |
| C(4)-C(5)-O(2)        | 111.1 (4)     | 110.9 (4)  | 110.6 (4)  | 110.0 (4)  | 110.7 (5)  |
| C(5)-O(2)-C(2)        | 106.4 (3)     | 106.0 (3)  | 105.4 (3)  | 106.6 (3)  | 106.1 (5)  |
| O(2)-C(2)-C(1)        | 113.4 (3)     | 114.8 (3)  | 113.7 (3)  | 114.2 (3)  | 114.0 (6)  |
| O(2)-C(2)-C(3)        | 109.4 (3)     | 109.0 (4)  | 109.7 (3)  | 109.3 (4)  | 109.4 (3)  |
| C(2)'-C(1)'-C(1)-C(2) | 69.9 (5)      |            | 66.2 (5)   |            | 68.1   |
| C(2)'-C(1)'-C(1)-N    | -111.1 (4)    | -107.4 (4) | -110.9 (4) | -115.8 (4) | -111.3 (34)  |
| C(1)'-C(1)-N-O(1)     | -179.0 (3)    | 177.1 (3)  | 177.6 (3)  | -177.8 (3) | 179.5 (25)   |
| C(1)'-C(1)-C(2)-O(2)  | 7.7 (5)       | 6.9 (6)    | 16.0 (5)   | 2.8 (5)    | 8.4 (55)   |

Table 1 lists the atomic parameters, and Fig. 1 shows the thermal ellipsoids and numbering scheme for the model and bond lengths and bond angles for the benzene molecule. The atom labels are identical in the halves of each furildioxime which are denoted as *A*, *B*, *C* and *D*. Bond lengths, bond angles and some torsion angles are listed in Table 2 for the furildioxime molecules. The XRAY system (Stewart, 1976) and *MULTAN* (Germain, Main & Woolfson, 1971) were used for the crystallographic computations.

### Origin of the red color

The red color of the crystals used for data collection must be due to small amounts of an adsorbed or entrained Re species since there is no significant electron density larger than  $0.27 \text{ e \AA}^{-3}$  remaining in a  $\Delta F$  map calculated for the final model. Colorless crystals of furildioxime obtained from ether and benzene without any contact with  $\text{K}_2\text{ReCl}_6$  give a powder diffraction pattern identical to that generated from the three-dimensional data set for the red crystal, indicating that the red color is not an intrinsic characteristic of the furildioxime crystal.

### Discussion

The halves of the furildioxime molecule are chemically identical, and the bond lengths and angles for the four similar moieties in the asymmetric unit are tabulated and compared in Table 2. The bond lengths and angles are fairly consistent between the four half molecules. The standard deviations of the averages are two to three times the standard deviation of an individual observation, the latter being systematically underestimated due to the blocked least-squares refinement.

The bond lengths and angles are consistent with values obtained for other structures containing the furil and dioxime moieties (Carpy, Leger & Nuhrich, 1978; Filippakis & Schmidt, 1967; Gieren & Dederer, 1977).

Clearly the short C(2)-C(3) and C(4)-C(5) distances are indicative of considerable double-bond character. Also, the bond lengths C(3)-C(4) and C(1)-C(2) are somewhat shorter than expected for C-C single bonds, contributing to the planar nature of each half of the molecule. The r.m.s. distances from the least-squares planes through the four half molecules are 0.065, 0.029, 0.103 and 0.040 Å.

Co-planarity of the C-N-O plane and the five-membered ring and the resulting steric interactions between O(1) and C(3) could contribute to the opening

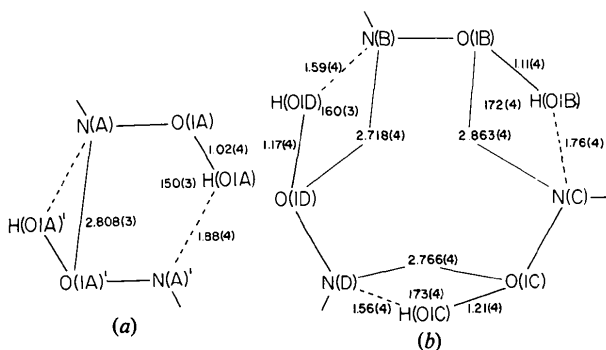


Fig. 2. A schematic diagram showing the hydrogen bonds. (a) The hydrogen bond between oxime groups related by a center of symmetry. (b) The hydrogen-bonding net formed by three oxime groups. (Distances are in Å.)

of the C(1)—C(2)—C(3) angle to over  $135^\circ$ . However, bonding effects within the five-membered ring itself must also play a role since the same effect is seen in other furil groups.

The oxime group is also in reasonable agreement with other structures reported in the literature, although the C—N distance is somewhat longer than normally found. The oximes in this study are all in the  $\alpha$  conformation as indicated by the torsion angles.

All four O—H groups in the asymmetric unit participate in hydrogen bonds with the four N atoms serving as acceptors. One of the oximes is hydrogen bonded to a centrosymmetrically related molecule, a bonding scheme commonly found in oxime structures (see Fig. 2a). The other three oxime groups are involved in the hydrogen-bonding pattern shown in Fig. 2(b).

Although the thermal parameters for the atoms in the benzene ring are considerably higher than for atoms in the rest of the structure, the bond lengths and bond angles for the ring are not unreasonable. The average

C—C distance is 1.356 Å and the average bond angle is  $120.0^\circ$ . Van der Waals interactions must account for the lack of complete rotational disorder in the benzene molecule. Due to the uncertainty in the location of the H atoms of the benzene molecule, the detailed interactions limiting the rotation cannot be accurately determined.

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