

# The Crystal Structure of Catena- $\mu$ -bromo[2-[[3-[(octahydropyrimido[2,1-*c*] [1,4]oxazin-9-yl)-amino]propyl]amino]ethanolato]-copper(II) Dibromo[2-[[3-[(octahydropyrimido[2,1-*c*] [1,4]oxazin-9-yl)-amino]propyl]amino]ethanol]copper(II) Sesquihydrate

Aarne Pajunen and Seija Pajunen

Division of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki 10, Finland

Pajunen, A. and Pajunen, S., 1986. The Crystal Structure of Catena- $\mu$ -bromo[2-[[3-[(octahydropyrimido[2,1-*c*] [1,4]oxazin-9-yl)amino]propyl]amino]ethanolato]-copper(II) Dibromo[2-[[3-[(octahydropyrimido[2,1-*c*] [1,4]oxazin-9-yl)amino]propyl]amino]ethanol]copper(II) Sesquihydrate. – Acta Chem. Scand. A 40: 413–417.

The crystal structure of the title compound, the end product of the reaction between  $\text{CuBr}_2$ , 2-[(3-aminopropyl)amino]ethanol and ethanedial (glyoxal), was determined by single crystal X-ray diffraction methods.  $[\text{CuBr}_2(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)] \cdot 1.5 \text{ H}_2\text{O}$  crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 11.059(12)$ ,  $b = 11.520(5)$ ,  $c = 28.604(16)$  Å,  $\beta = 95.04(4)^\circ$  and  $Z = 4$ . The structure was refined to  $R = 0.057$  from 2145 observed reflections. The asymmetric unit consists of two different six-coordinate complexes and 1.5 solvent molecules. In one complex, the ligand coordinates as a neutral molecule; the two apical sites are occupied by two bromide ions. In the second complex, the ligand coordinates in the deprotonated form with a single bromide ion lying between two complexes, giving rise to a polymeric chain.

Crystal structures of complexes formed by Cu(II) ion and 2-[(3-aminopropyl)amino]ethanol (HL) have been extensively studied in recent years.<sup>1–7</sup> To prepare complexes of Schiff bases derived from this ligand and aliphatic carbonyl compounds, we studied the system  $\text{CuBr}_2/\text{HL}/\text{ethanedial}$  (glyoxal). We report here the results of an X-ray structural examination of the end-product of the reaction of these compounds – a complex of unexpected chemical composition.

## Experimental

The complex was prepared by mixing a hot aqueous solution of ethanedial with an ethanolic solution containing 2-[(3-aminopropyl)amino]ethanol and, after cooling, adding  $\text{CuBr}_2$  in methanol; mole ratio 1:2:1. The blue crystalline product was obtained by slow evaporation.

Both the crystal and intensity data were measured on an automatic Nicolet P3 four-circle dif-

Table 1. Crystal data.

---

|   |
|---|
| $[\text{CuBr}(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)] [\text{CuBr}_2(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)] \cdot 1.5 \text{ H}_2\text{O}$ , $F.W. = 909.55$ , monoclinic, $a = 11.059(12)$ , $b = 11.520(5)$ , $c = 28.604(16)$ Å, $\beta = 95.04(4)^\circ$ , $V = 3630.1$ Å <sup>3</sup> , $D_m = 1.69$ (floatation), $D_x = 1.66$ gcm <sup>-3</sup> , $Z = 4$ , $F(000) = 1844$ , $\mu(\text{MoK}\alpha) = 44.9$ cm <sup>-1</sup> , $T = 298$ K, space group $P2_1/c$ |
|---|

---

fractometer using graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107$  Å). The cell dimensions were obtained by least squares refinement of setting angles for 12 well centred reflections. Crystal data are presented in Table 1; experimental data and structure refinement parameters are summarized in Table 2. The intensities of two standard reflections recorded after every 50 measurements showed no significant variation. Data were corrected for Lorentz and polarization effects and for absorption from  $\Phi$ -scan data.<sup>8</sup>

Table 2. Experimental data and structure refinement parameters.

|   |   |
|---|---|
| Crystal size (mm <sup>3</sup> )                             | 0.2×0.2×0.4   |
| Transmission factors  | 1.00–0.62   |
| Scan speed (° min <sup>-1</sup> )                           | 1.5–29.3  |
| Range of <i>h,k,l</i>                                       | 0 ≤ <i>h</i> ≤ 12<br>0 ≤ <i>k</i> ≤ 13<br>-31 ≤ <i>l</i> ≤ 31 |
| 2θ (°)  | 3 < 2θ < 45   |
| Number of reflections measured                              | 5042  |
| Number of reflections observed ( <i>I</i> > 2σ( <i>I</i> )) | 2145  |
| Number of parameters refined                                | 386   |
| Quantity minimized  | $\sum w   F_o  -  F_c  ^2$                                    |
| Weighting scheme  | $w = (\sigma(F))^{-1}$  |
| $R = \sum   F_o  -  F_c   / \sum  F_o $                     | 0.057   |
| $R_w = (\sum w   F_o  -  F_c  ^2 / (\sum w  F_o ^2))^{1/2}$ | 0.065   |

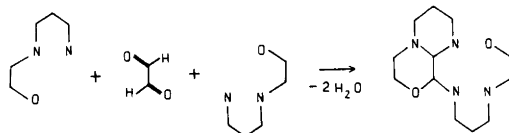
#### Structure determination and refinement

The positions of Br and Cu atoms were determined by direct methods (MULTAN).<sup>9</sup> The other non-hydrogen ligand atoms were located from successive Fourier syntheses. In the calculation of  $F_c$ , atomic scattering factors from Cromer and Mann<sup>10</sup> were used for non-hydrogen atoms and those from Stewart *et al.*<sup>11</sup> for H atoms. The anomalous dispersion coefficients for Br and Cu were included in the calculations.<sup>12</sup> The difference map showed two maxima belonging to the oxygen atoms of the water. Although most of the H atoms of the ligand molecules were found in the difference synthesis, their positions were calculated geometrically. They were included in the subsequent refinements at fixed positions with a fixed U value of 0.06 Å<sup>2</sup>. The H atoms of the water molecules could not be located. The computations were performed with the X-Ray 76 system;<sup>13</sup> the figure was drawn with the PLUTO program.<sup>14</sup>

Lists of coordinates of hydrogen atoms, anisotropic thermal parameters and observed and calculated structural factors can be obtained from the authors on request.

## Results and discussion

The atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 3. The bond lengths and angles are listed in Table 4. The labelling of the atoms and a perspective view of the complexes are shown in Fig. 1. The ligand molecule is formed by condensation of 2 moles of 2-[(3-aminopropyl)amino]ethanol and 1 mole of ethanedial.



One diaminoalcohol molecule and one ethanedial molecule form the octahydropyrimido[2,1-*c*][1,4]oxazin moiety. The asymmetric unit consists of two different six-coordinate complexes and 1.5 solvent water molecules. The coordination around each Cu(II) ion is a tetragonally distorted octahedral (4 + 2) coordination with three N atoms and one O atom in the basal plane and Br ions in the apical positions. The interatomic dis-

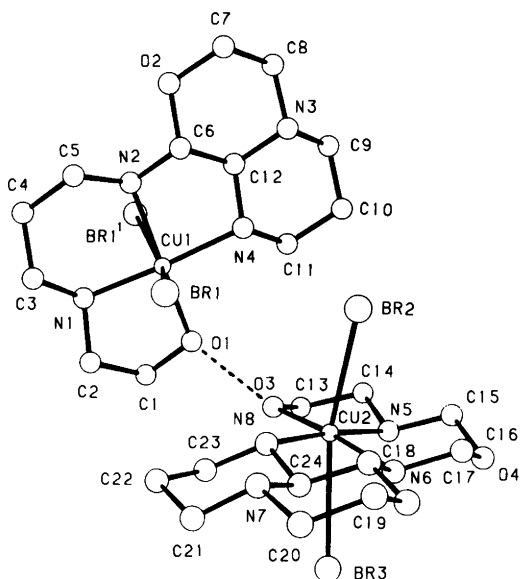


Fig. 1. Numbering scheme and arrangement of the two complexes viewed along the *b* axis. Dashed line indicates the O(1) ... H - O(3) hydrogen bond.

Table 3. Fractional atomic coordinates and  $U_{eq}$  for the nonhydrogen atoms, with e.s.d.'s in parentheses.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| Atom  | x           | y           | z          | $U_{eq}$  |
|-------|-------------|-------------|------------|-----------|
| Br(1) | 0.4623(2)   | 0.3465(2)   | 0.2128(1)  | 0.048(1)  |
| Br(2) | 0.0915(2)   | 0.2814(2)   | 0.1864(1)  | 0.059(1)  |
| Br(3) | 0.1445(2)   | 0.1529(2)   | -0.0140(1) | 0.056(1)  |
| Cu(1) | 0.4718(3)   | 0.1021(2)   | 0.2356(1)  | 0.036(2)  |
| Cu(2) | 0.1413(3)   | 0.1986(2)   | 0.0937(1)  | 0.045(2)  |
| O(1)  | 0.4139(12)  | 0.0470(10)  | 0.1734(4)  | 0.036(7)  |
| O(2)  | 0.4506(12)  | 0.1946(10)  | 0.3738(4)  | 0.037(8)  |
| O(3)  | 0.2453(12)  | 0.0701(10)  | 0.1143(4)  | 0.048(8)  |
| O(4)  | 0.0455(13)  | 0.5374(10)  | 0.0556(4)  | 0.058(8)  |
| O(5)  | 0.1650(14)  | 0.3772(11)  | 0.2953(5)  | 0.068(11) |
| O(6)  | 0.5         | 0.0         | 0.0        | 0.108(33) |
| N(1)  | 0.6392(14)  | 0.0747(11)  | 0.2171(4)  | 0.035(9)  |
| N(2)  | 0.5339(14)  | 0.1382(11)  | 0.3031(4)  | 0.035(8)  |
| N(3)  | 0.2112(15)  | 0.1361(13)  | 0.3325(5)  | 0.041(9)  |
| N(4)  | 0.3036(15)  | 0.1057(11)  | 0.2593(4)  | 0.041(8)  |
| N(5)  | 0.0075(14)  | 0.0807(12)  | 0.0858(4)  | 0.046(9)  |
| N(6)  | 0.0361(13)  | 0.3314(12)  | 0.0662(4)  | 0.040(9)  |
| N(7)  | 0.3020(15)  | 0.5193(12)  | 0.0759(5)  | 0.043(10) |
| N(8)  | 0.2741(13)  | 0.3171(11)  | 0.0951(4)  | 0.031(11) |
| C(1)  | 0.5131(19)  | 0.0079(14)  | 0.1494(6)  | 0.042(11) |
| C(2)  | 0.6271(20)  | 0.0774(16)  | 0.1651(6)  | 0.051(13) |
| C(3)  | 0.7358(20)  | 0.1542(17)  | 0.2363(6)  | 0.057(13) |
| C(4)  | 0.7547(19)  | 0.1536(17)  | 0.2884(6)  | 0.050(14) |
| C(5)  | 0.6449(18)  | 0.2073(16)  | 0.3104(6)  | 0.049(14) |
| C(6)  | 0.4306(16)  | 0.1839(14)  | 0.3238(5)  | 0.029(13) |
| C(7)  | 0.3416(18)  | 0.2289(17)  | 0.3947(6)  | 0.045(15) |
| C(8)  | 0.2396(19)  | 0.1424(17)  | 0.3830(6)  | 0.047(15) |
| C(9)  | 0.1190(20)  | 0.0476(17)  | 0.3193(7)  | 0.061(16) |
| C(10) | 0.0916(19)  | 0.0361(16)  | 0.2679(7)  | 0.047(16) |
| C(11) | 0.2070(19)  | 0.0172(15)  | 0.2444(6)  | 0.038(15) |
| C(12) | 0.3200(18)  | 0.1052(14)  | 0.3103(5)  | 0.031(12) |
| C(13) | 0.1790(19)  | -0.0363(16) | 0.1082(6)  | 0.052(13) |
| C(14) | 0.0460(18)  | -0.0200(16) | 0.1154(6)  | 0.052(15) |
| C(15) | -0.1160(18) | 0.1165(17)  | 0.0950(6)  | 0.048(16) |
| C(16) | -0.1555(19) | 0.2184(18)  | 0.0643(7)  | 0.058(16) |
| C(17) | -0.0919(20) | 0.3326(17)  | 0.0767(6)  | 0.059(16) |
| C(18) | 0.0962(18)  | 0.4362(15)  | 0.0793(6)  | 0.131(15) |
| C(19) | 0.1149(21)  | 0.6376(17)  | 0.0678(7)  | 0.081(16) |
| C(20) | 0.2370(22)  | 0.6242(16)  | 0.0536(6)  | 0.078(16) |
| C(21) | 0.4173(22)  | 0.4957(17)  | 0.0571(6)  | 0.056(16) |
| C(22) | 0.4825(21)  | 0.3863(19)  | 0.0798(6)  | 0.051(17) |
| C(23) | 0.3911(18)  | 0.2837(15)  | 0.0792(7)  | 0.047(15) |
| C(24) | 0.2210(7)   | 0.4182(14)  | 0.0680(5)  | 0.066(17) |

tances between the Cu(II) ion and the basal atoms (1.93(1)–2.04(1) Å) are typical for coordination bonds. Most of the bond lengths and bond angles are closely similar for the two complexes. The main differences occur in the coordination of the OH group and Br ions. In one complex, the

ligand coordinates as a neutral molecule, the apical sites being occupied by two Br ions with Cu–Br distances of 2.915(3) and 3.130(3) Å. In the second complex, the ligand coordinates in the deprotonated form; the apical Br ion is shared by two complexes to give rise to a polymeric chain.

Table 4. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

|                                |          |                   |          |
|--------------------------------|----------|-------------------|----------|
| Cu(1)–Br(1)                    | 2.890(3) | Cu(2)–Br(2)       | 2.915(3) |
| Cu(1)–Br(1) <sup>1</sup>       | 3.346(3) | Cu(2)–Br(3)       | 3.130(3) |
| Cu(1)–O(1)                     | 1.95(1)  | Cu(2)–O(3)        | 1.93(1)  |
| Cu(1)–N(1)                     | 1.99(2)  | Cu(2)–N(5)        | 2.01(2)  |
| Cu(1)–N(2)                     | 2.03(1)  | Cu(2)–N(6)        | 2.04(1)  |
| Cu(1)–N(4)                     | 2.03(2)  | Cu(2)–N(8)        | 2.00(1)  |
| O(1)–C(1)                      | 1.42(2)  | O(3)–C(13)        | 1.43(2)  |
| C(1)–C(2)                      | 1.53(3)  | C(13)–C(14)       | 1.51(3)  |
| C(2)–N(1)                      | 1.48(2)  | C(14)–N(5)        | 1.48(2)  |
| N(1)–C(3)                      | 1.48(2)  | N(5)–C(15)        | 1.47(3)  |
| C(3)–C(4)                      | 1.49(2)  | C(15)–C(16)       | 1.51(3)  |
| C(4)–C(5)                      | 1.55(3)  | C(16)–C(17)       | 1.52(3)  |
| C(5)–N(2)                      | 1.46(2)  | C(17)–N(6)        | 1.47(3)  |
| N(2)–C(6)                      | 1.43(2)  | N(6)–C(18)        | 1.41(2)  |
| C(6)–O(2)                      | 1.43(2)  | C(18)–O(4)        | 1.44(2)  |
| O(2)–C(7)                      | 1.45(2)  | O(4)–C(19)        | 1.41(2)  |
| C(7)–C(8)                      | 1.52(3)  | C(19)–C(20)       | 1.45(3)  |
| C(8)–N(3)                      | 1.45(2)  | C(20)–N(7)        | 1.52(2)  |
| N(3)–C(12)                     | 1.45(2)  | N(7)–C(24)        | 1.47(2)  |
| C(12)–C(6)                     | 1.54(2)  | C(24)–C(18)       | 1.46(3)  |
| N(3)–C(9)                      | 1.47(3)  | N(7)–C(21)        | 1.45(3)  |
| C(9)–C(10)                     | 1.48(3)  | C(21)–C(22)       | 1.57(3)  |
| C(10)–C(11)                    | 1.51(3)  | C(22)–C(23)       | 1.55(3)  |
| C(11)–N(4)                     | 1.51(2)  | C(23)–N(8)        | 1.46(3)  |
| N(4)–C(12)                     | 1.46(2)  | N(8)–C(24)        | 1.49(2)  |
| N(1)–Cu(1)–O(1)                | 86.8(5)  | N(5)–Cu(2)–O(3)   | 85.9(6)  |
| N(1)–Cu(1)–N(2)                | 92.3(6)  | N(5)–Cu(2)–N(6)   | 94.2(6)  |
| N(2)–Cu(1)–N(4)                | 85.6(6)  | N(6)–Cu(2)–N(8)   | 83.6(6)  |
| N(4)–Cu(1)–O(1)                | 84.2(5)  | N(8)–Cu(2)–O(3)   | 95.8(5)  |
| Br(1)–Cu(1)–O(1)               | 96.2(3)  | Br(2)–Cu(2)–O(3)  | 97.4(3)  |
| Br(1)–Cu(1)–N(1)               | 96.3(4)  | Br(2)–Cu(2)–N(5)  | 97.3(4)  |
| Br(1)–Cu(1)–N(2)               | 91.0(4)  | Br(2)–Cu(2)–N(6)  | 87.6(4)  |
| Br(1)–Cu(1)–N(4)               | 92.3(4)  | Br(2)–Cu(2)–N(8)  | 87.5(4)  |
| Br(1) <sup>1</sup> –Cu(1)–O(1) | 99.1(3)  | Br(3)–Cu(2)–O(3)  | 96.3(3)  |
| Br(1) <sup>1</sup> –Cu(1)–N(1) | 78.8(4)  | Br(3)–Cu(2)–N(5)  | 81.1(4)  |
| Br(1) <sup>1</sup> –Cu(1)–N(2) | 73.7(4)  | Br(3)–Cu(2)–N(6)  | 78.7(4)  |
| Br(1) <sup>1</sup> –Cu(1)–N(4) | 92.3(4)  | Br(3)–Cu(2)–N(8)  | 93.7(4)  |
| Cu(1)–O(1)–C(1)                | 110(1)   | Cu(2)–O(3)–C(15)  | 110(1)   |
| O(1)–C(1)–C(2)                 | 110(1)   | O(3)–C(13)–C(14)  | 112(1)   |
| C(1)–C(2)–N(1)                 | 106(2)   | C(13)–C(14)–N(5)  | 105(1)   |
| Cu(1)–N(1)–C(2)                | 105(1)   | Cu(2)–N(5)–C(14)  | 107(1)   |
| Cu(1)–N(1)–C(3)                | 117(1)   | Cu(2)–N(5)–C(15)  | 118(1)   |
| C(2)–N(1)–C(3)                 | 111(1)   | C(14)–N(5)–C(15)  | 110(1)   |
| N(1)–C(3)–C(4)                 | 114(2)   | N(5)–C(15)–C(16)  | 110(2)   |
| C(3)–C(4)–C(5)                 | 111(2)   | C(15)–C(16)–C(17) | 116(2)   |
| C(4)–C(5)–N(2)                 | 114(1)   | C(16)–C(17)–N(6)  | 112(2)   |
| Cu(1)–N(2)–C(5)                | 117(1)   | Cu(2)–N(6)–C(17)  | 117(1)   |
| Cu(1)–N(2)–C(6)                | 105(1)   | Cu(2)–N(6)–C(18)  | 107(1)   |
| C(5)–N(2)–C(6)                 | 116(1)   | C(17)–N(6)–C(18)  | 112(1)   |
| N(2)–C(6)–O(2)                 | 113(1)   | N(6)–C(18)–O(4)   | 114(1)   |
| N(2)–C(6)–C(12)                | 109(1)   | N(6)–C(18)–C(24)  | 105(1)   |
| C(12)–C(6)–O(2)                | 110(1)   | C(24)–C(18)–O(4)  | 110(1)   |
| C(6)–O(2)–C(7)                 | 112(1)   | C(18)–O(4)–C(19)  | 112(1)   |

(Cont. next page)

Table 4. (cont.)

|                  |        |                   |        |
|------------------|--------|-------------------|--------|
| O(2)–C(7)–C(8)   | 111(1) | O(4)–C(19)–C(20)  | 110(2) |
| C(7)–C(8)–N(3)   | 110(1) | C(19)–C(20)–N(7)  | 113(2) |
| C(8)–N(3)–C(12)  | 109(1) | C(20)–N(7)–C(24)  | 108(1) |
| C(8)–N(3)–C(9)   | 112(1) | C(20)–N(7)–C(21)  | 113(1) |
| C(9)–N(3)–C(12)  | 108(1) | C(21)–N(7)–C(24)  | 110(1) |
| N(3)–C(9)–C(10)  | 113(2) | N(7)–C(21)–C(22)  | 113(2) |
| C(9)–C(10)–C(11) | 110(2) | C(21)–C(22)–C(23) | 109(2) |
| C(10)–C(11)–N(4) | 112(1) | C(22)–C(23)–N(7)  | 113(1) |
| Cu(1)–N(4)–C(11) | 122(1) | Cu(2)–N(8)–C(23)  | 119(1) |
| Cu(1)–N(4)–C(12) | 107(1) | Cu(2)–N(8)–C(24)  | 106(1) |
| C(11)–N(4)–C(12) | 108(1) | C(23)–N(8)–C(24)  | 111(1) |
| N(4)–C(12)–N(3)  | 114(1) | N(8)–C(24)–N(7)   | 109(1) |
| N(4)–C(12)–C(6)  | 106(1) | N(8)–C(24)–C(18)  | 109(1) |
| N(3)–C(12)–C(6)  | 115(1) | N(7)–C(24)–C(18)  | 115(1) |

Equivalent position  $1-x, -\frac{1}{2}-y, \frac{1}{2}-z$

The distance Cu(1)–Br(1) of 2.890(3) Å indicates strong interaction between the ions, while the Cu(1)–Br(1) ( $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ) distance of 3.346 Å, which is longer than the sum of the ionic radii of Cu<sup>2+</sup> and Br<sup>-</sup> (3.23 Å),<sup>15</sup> indicates only weak interaction.

Both complexes contain three six-membered and two five-membered rings. All six-membered rings are in a *chair* conformation, all five-membered rings are *gauche*. The difference in the coordination has an effect on the deviations of the Cu ions from the least squares planes through the four basal atoms. Cu(1) deviates 0.139(7) Å towards Br(1) while Cu(2) deviates only 0.087(7) Å towards Br(2). The complexes are bound together by a short hydrogen bond (2.42(2) Å) between O(1) and O(3). The water molecules are situated in cavities between the complexes and do not participate in hydrogen bonding.

## References

- Pajunen, A. and Nieminen, K. *Finn. Chem. Lett.* (1975) 67.
- Nieminen, K. *Acta Chem. Scand. A 31* (1977) 693.
- Nieminen, K. and Pajunen, A. *Acta Chem. Scand. A 32* (1978) 493.
- Nieminen, K. *Acta Chem. Scand. A 33* (1979) 375.
- Nieminen, K. and Näsäkkälä, M. *Acta Chem. Scand. A 34* (1980) 375.
- Nieminen, K. *Acta Chem. Scand. A 35* (1981) 753.
- Nieminen, K. *Ann. Acad. Sci. Finn. A II* (1983).
- North, A. C. T., Phillips, D. C. and Mathews, F. S. *Acta Crystallogr. A 24* (1968) 351.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. and Woolfson, M. M. *MULTAN 80: A System for Automatic Solution of Crystal Structures from X-Ray Diffraction Data*. University of York, York, UK 1980.
- Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A 24* (1968) 321.
- Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK 1978, Vol. 4 p. 72.
- Stewart, J. M. *The X-Ray System, Version of 1976, Technical Report TR-446*, University of Maryland, College Park, MD 1976.
- Motherwell, W. D. S. *PLUTO: Program for Plotting Crystal and Molecular Structures*, University of Cambridge, Cambridge, UK 1976.
- Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York 1960, pp. 160, 252, 260.

Received February 26, 1986.