

The Crystal and Molecular Structure of Bis(*ortho*-aminobenzoato)copper(II), $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ *

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Received December 9, 1974

Bis (*ortho*-aminobenzoato)copper (II), $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$, crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 12.95$ (1), $b = 5.25$ (1), $c = 9.39$ (1) Å, and $\beta = 93.3$ (1)°. The structure was determined using three-dimensional X-ray diffraction data gathered on multiple-film, equi-inclination, integrated Weissenberg photographs taken about two crystal axes. Refinement, with anisotropic temperature factors, led to $R = 3.1\%$. Coordination about the copper is that of a distorted octahedron. Four equatorial positions are occupied by two amino nitrogens and two carboxylate oxygens with both the nitrogens and oxygens in *trans* positions. The octahedral coordination is completed in the axial positions by two carbonyl oxygens which do not originate from the same ligands that occupy the equatorial sites. Each copper in the (100) plane is attached to four other coppers via carboxylate bridges to give a two-dimensional polymeric network coincident with the (100) plane. Significant hydrogen bonding occurs to strengthen the two-dimensional network, which, it is suggested, accounts for the extreme insolubility and high thermal stability of the compound.

Introduction

Ortho-aminobenzoic acid (anthranilic acid) is an important precursor to tryptophan, one of the 20 biologically important *alpha* amino acids. *Ortho*-aminobenzoic acid is a *beta* amino acid and in view of the extreme interest that has recently developed in amino acid and peptide complexes with various metal ions, it was felt that a study of the complexation characteristics of this amino acid was warranted. *Ortho*-aminobenzoic acid forms stable, highly insoluble compounds with numerous divalent and trivalent metals, and has been used as a reagent for quantitative determinations of these metals (1, 2).

Several spectroscopic studies have been performed on the divalent metal *ortho*-

aminobenzoates in an effort to elucidate their structure, but the results of these studies are at variance. Sandhu et al. (3) propose a structure in which the *ortho*-aminobenzoate acts as a tridentate ligand, giving rise to a distorted octahedral coordination about the central metal. Khakimov et al. (4) also conclude that the compounds have a distorted octahedral structure. Hill and Curran (5) and Decker and Frye (6) advocate a square planar structure in which the *ortho*-aminobenzoate is bidentate.

All three aminobenzoic acids form complexes with copper (II), with significantly different structures. Work on the *meta* and *para* compounds is in progress, and comparisons should prove interesting.

Experimental

Single crystals of $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ were prepared by a method of diffusion mentioned by Bunn (7). Aqueous solutions of copper sulfate and the sodium salt of *ortho*-amino-

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benzoic acid were placed in separate flasks, and over a 2-month period the reactants were allowed to diffuse toward each other through an aqueous medium. The small, flat, dark green, diamond-shaped crystals formed predominantly in the copper sulfate flask and were removed by filtration.

Preliminary Weissenberg photographs showed the crystals to be monoclinic. Systematic absences of $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$ indicated the space group $P2_1/c$. Intensity statistics indicated a centrosymmetric structure, further confirming $P2_1/c$.

The unit cell dimensions were determined using zero level Weissenberg photographs and rotation photographs taken about $[100]$, $[010]$, $[001]$ using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). All measurements were made at 21° . The pertinent data are given in Table I. The observed density of $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ corresponds to two formula units per unit cell. The density measurements were made pycnometrically with an aqueous soap solution of known density to insure wetting of the $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ powder.

Intensity data for $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ were gathered with Ni-filtered $\text{CuK}\alpha$ radiation using multiple-film, equi-inclination, integrated Weissenberg photographs for layers 0–3 of a crystal mounted on the b -axis, and

layers 0–4 of a crystal mounted on the c -axis. Four Kodak No-Screen medical X-ray films were used for each layer, the average film absorption factor being 3.8 (2). The dimensions of the crystals were $0.07 \times 0.18 \times 0.11 \text{ mm}$ and $0.06 \times 0.15 \times 0.07 \text{ mm}$ respectively as referred to $[100]$, $[010]$, $[001]$. The intensities of the reflections were measured with a Welch Densichron for which a 0.5 mm aperture was made. The photometer was calibrated with a standard density wedge. The intensities were corrected for Lorentz and polarization factors, and the two sets of relative intensities were cross scaled and correlated using the method of Hamilton (8). The value of the linear absorption coefficient, μ , with copper radiation for $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ is 26.52 cm^{-1} and, in view of the small magnitude of μ , no correction for absorption was made. A scale factor to place the relative intensities on an absolute scale and a value for the overall temperature factor, B , were derived with a Wilson plot. 445 nonzero reflections were recorded, a nonzero reflection being defined as a diffraction spot visible on any film.

Structure Determination and Refinement

Three-dimensional, sharpened Patterson functions were used to locate the copper atom and two of the oxygen atoms. The remaining nonhydrogen atoms were then located on three-dimensional Fourier maps. The initial refinement of the structure was made using the least-squares method with a block diagonal approximation. This refinement on all nonhydrogen atoms and their isotropic temperature factors yielded an R -value of 0.056 after four cycles. Residuals quoted are

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

Further refinement using full matrix least-squares calculations with anisotropic temperature factors for all nonhydrogen atoms, and copper scattering factors corrected for anomalous dispersion, lowered R to 0.044. At this stage a difference map was generated, and all six hydrogen atoms were readily found. The average amplitude of the hydrogen peaks was $0.4 \text{ e}/\text{\AA}^3$. An additional three cycles of

TABLE I
CRYSTALLOGRAPHIC DATA

Symmetry	Monoclinic
Cell dimensions	$a = 12.95 (1) \text{ \AA}$ $b = 5.25 (1) \text{ \AA}$ $c = 9.39 (1) \text{ \AA}$ $\beta = 93.3 (1)^\circ$
Cell volume	637.4 \AA^3
Formula weight	335.80
Z	2
Density (measured)	1.75
Density (X-ray)	1.749
Absorption coefficient ^a , μ	26.52 cm^{-1}
Systematic absences	$h0l: l = 2n + 1$ $0k0: k = 2n + 1$
Space group	$P2_1/c$

^a For copper radiation.

refinement (full matrix), including these hydrogen atoms, to which constant isotropic temperature factors of 5.0 were assigned, gave a final R -value of 0.031. In the final cycle, the ratio of the largest shift to the standard deviation in the coordinate was less than 0.3. A final difference map showed no peaks with an intensity greater than $0.29 \text{ e}/\text{\AA}^3$. A full correlation matrix showed no elements greater than 0.39, and an error analysis revealed no systematic errors as a function of either $\sin^2\theta$ or F_{obs} . The error analysis also indicated that all but six reflections had $||F_{\text{obs}}| - |F_{\text{calc}}||/|F_{\text{obs}}|$ less than twice the final R -value, or $||F_{\text{obs}}| - |F_{\text{calc}}||$ less than one-half the $|F_{\text{obs}}|$ value of the weakest reflection.

In both the block diagonal and full matrix least-squares procedures the function minimized was $\sum W(|F_o| - |F_c|)^2$; $W = 1/\sigma^2(|F_o|)$. The atomic scattering factors for the non-hydrogen atoms were taken from those tabulated by Hanson (9), while those for hydrogen were from Stewart (10). Corrections for anomalous dispersion were made only for copper, and the values of $\Delta f'$ and $\Delta f''$ (-2.15 and 0.75), were those given in a report by Cromer (11). The values of the refined parameters and their estimated standard deviations are listed in Table II. A tabulation of the observed structure factors and the final

TABLE IIA

FINAL POSITIONAL AND THERMAL PARAMETERS:
POSITIONAL PARAMETERS^{a, b}

Atom	x	y	z
Cu	0.00000 (0)	0.00000 (0)	0.00000 (0)
O(1)	0.0340 (4)	0.1858 (10)	0.1792 (5)
O(2)	0.1273 (4)	0.2556 (10)	0.3806 (5)
N(1)	0.1032 (5)	0.7331 (13)	0.0714 (6)
C(1)	0.1179 (6)	0.1708 (14)	0.2568 (7)
C(2)	0.2112 (6)	0.0536 (14)	0.1975 (8)
C(3)	0.2037 (6)	0.8404 (15)	0.1070 (7)
C(4)	0.2905 (7)	0.7388 (17)	0.0499 (9)
C(5)	0.3871 (7)	0.8480 (19)	0.0819 (10)
C(6)	0.3957 (7)	0.0524 (21)	0.1727 (10)
C(7)	0.3094 (6)	0.1543 (18)	0.2312 (8)
H(1)	0.119 (7)	0.621 (18)	0.010 (10)
H(2)	0.074 (8)	0.691 (19)	0.146 (10)
H(4)	0.287 (7)	0.601 (18)	0.987 (9)
H(5)	0.449 (7)	0.787 (19)	0.033 (9)
H(6)	0.462 (7)	0.134 (18)	0.202 (9)
H(7)	0.313 (8)	0.275 (19)	0.229 (10)

^a The anisotropic thermal parameter is defined as $f = f_0 \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

^b Estimated standard deviations are given in parentheses; x , y , and z are fractional coordinates.

TABLE IIB

FINAL POSITIONAL AND THERMAL PARAMETERS:
ANISOTROPIC THERMAL PARAMETERS ($\times 10^4 \text{ \AA}^2$)^a

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	226.0 (8.5)	159.1 (8.7)	153.3 (7.6)	16.7 (7.4)	-15.4 (2.8)	-3.0 (6.1)
O(1)	209.9 (29.6)	223.4 (33.5)	164.0 (27.2)	-0.7 (13.4)	-4.9 (11.4)	0.7 (12.7)
O(2)	342.8 (33.9)	277.7 (33.6)	180.0 (27.6)	6.4 (14.1)	-8.9 (12.3)	-56.2 (13.2)
N(1)	200.6 (38.1)	215.5 (45.1)	202.7 (42.8)	10.1 (15.8)	17.5 (16.3)	-5.6 (15.0)
C(1)	232.8 (45.7)	81.9 (51.4)	221.4 (41.4)	16.5 (19.6)	8.6 (17.8)	19.2 (19.1)
C(2)	221.8 (41.5)	96.0 (67.3)	160.0 (38.8)	2.1 (18.0)	9.2 (15.0)	26.1 (17.8)
C(3)	220.9 (46.6)	173.3 (51.4)	137.2 (40.1)	-7.2 (20.6)	-7.7 (16.6)	42.0 (19.0)
C(4)	345.4 (54.2)	258.9 (55.7)	310.6 (50.3)	62.7 (22.5)	19.3 (21.5)	8.1 (20.3)
C(5)	235.3 (55.0)	487.0 (66.8)	402.8 (58.4)	24.6 (25.8)	19.3 (22.1)	-22.6 (27.3)
C(6)	265.8 (51.6)	517.6 (100.7)	428.2 (53.9)	-12.0 (27.2)	14.1 (20.9)	0.6 (27.4)
C(7)	258.2 (49.9)	339.1 (58.1)	245.5 (47.2)	-25.4 (24.1)	-7.7 (19.3)	-8.9 (21.7)

^a See footnotes to Table IIA.

calculated structure factors is given in Table III.

Results and Discussion

The contents of one unit cell for $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ are shown in Fig. 1, and the coordination around copper is shown in Fig. 2. Each copper atom has distorted octahedral coordination. Each *ortho*-aminobenzoate group functions as a tridentate ligand, but the three sites of attachment on the ligand are not associated with the same copper atom. The amino nitrogen, N(1), and the carboxylate oxygen, O(1), coordinate the copper equatorially and are *cis* to each other. The axial positions of the distorted octahedron are occupied by two carbonyl oxygens, O(2), each of which belongs to a different *ortho*-aminobenzoate ligand, the ligands being related by the center of symmetry at the copper atom. Thus, four *ortho*-aminobenzoate residues are associated with each copper. The result of this mode of coordination is that each copper in the (100) plane is attached to four other coppers via carboxylate bridges to give a two-dimensional polymeric sheet structure coincident with (100). This two-dimensional network is illustrated in Fig. 3. This arrangement is similar to one found in copper *gamma*-aminobutyrate dihydrate where the entire molecule serves as a bridge (12). The aromatic

rings of the *ortho*-aminobenzoate extend in a nearly perpendicular manner on either side of the sheets and may provide lateral stability. The polymeric structure may be the source of the extreme insolubility of the compound.

In this structure, hydrogen bonding occurs between the amino nitrogen, N(1), and a carbonyl oxygen, O(2), in an adjacent molecule and is represented by the dotted lines shown in Fig. 3. The N(1)–O(2) distance is 3.155 (8) Å and the N(1)–H(1)···O(2) angle is 162 (8)°. This length is well within the range found for hydrogen bonds formed between amine groups and oxygen (2.57–3.22 Å). The angle being within 30° of a straight line further confirms that it is a satisfactory hydrogen bond (13). Thus, the hydrogen bonding provides additional cross-linking in the polymeric network and, in conjunction with the bridging configuration, determines the packing of the molecules.

The bond distances and angles found in bis(*ortho*-aminobenzoato)copper(II) are listed in Table IV. The axial bond length of Cu–O(2) (2.415 Å) is noticeably longer than the equatorial bond lengths of Cu–O(1) (1.973 Å) and Cu–N(1) (2.024 Å), as would be expected with the Jahn–Teller effect in operation. The C–O distances in the carbonyl group are significantly different (C(1)–O(1) = 1.276 Å, C(1)–O(2) = 1.244 Å), an indication that the *pi* delocalization between these bonds is not

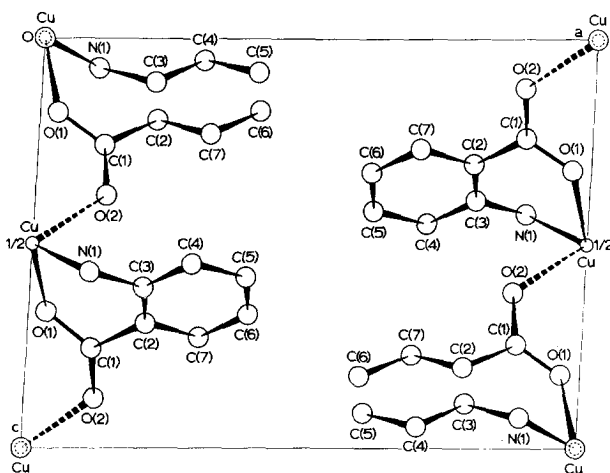


FIG. 1. The contents of one unit cell for $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ as viewed along [010].

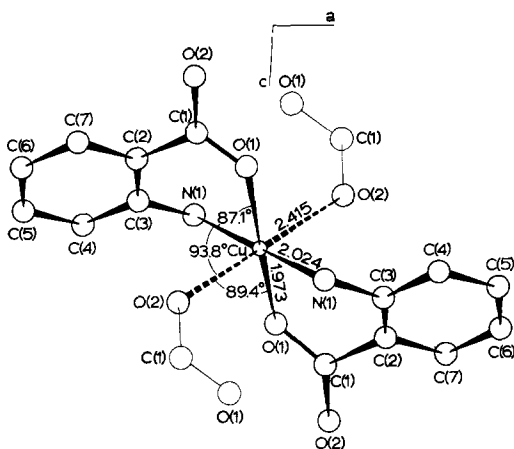


FIG. 2. The distorted octahedral coordination of the copper atom as viewed along [010].

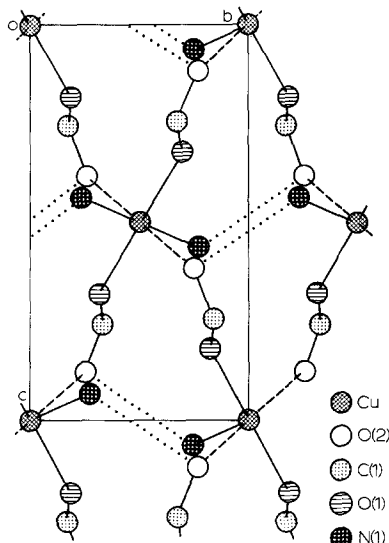


FIG. 3. The two dimensional polymeric network found in the *bc* plane of $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$.

equal—undoubtedly a consequence of the bonding configuration. The $\text{C}(1)\text{—O}(2)\text{—Cu}$ and $\text{C}(3)\text{—N}(1)\text{—Cu}$ bond angles (126.3° and 112.1°) support sp^2 and sp^3 hybridization of $\text{O}(2)$ and $\text{N}(1)$, respectively. However, the 126.7° magnitude of the $\text{C}(1)\text{—O}(1)\text{—Cu}$ angle is somewhat larger than that expected for sp^3 hybridization and may result from the rigidity of the organic ligand or partial π delocalization. The $\text{Cu}\text{—N}(1)$ and $\text{Cu}\text{—O}(1)$ distances and

the $\text{N}(1)\text{—Cu}\text{—O}(1)$ angle are comparable with the corresponding average values, 2.00 (8), 1.96 (6) Å, and 84° , obtained from a large number of reported copper (II) complexes with amino acids and peptides (14). The planarity of the two amino nitrogens and the two carboxylate oxygens is required by symmetry, i.e., the center of symmetry located at the copper atom. This plane is defined by the normal equation: $0.7452X + 0.4897Y + 0.4374Z = 0.0$, where X , Y , and Z are the orthogonalized atomic coordinates in Ångstroms and the coefficients are the direction cosines of the normal to the plane. The distance of the carbonyl oxygen from this plane is 2.410 Å.

A thermal ellipsoid drawing of one molecule of $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ is depicted in Fig. 4, the axial oxygens, $\text{O}(2)$, having been omitted since, strictly speaking, they are not part of the molecule. A number of interesting features are revealed in this drawing. Those atoms on the periphery of the molecule, i.e., $\text{C}(4)$, $\text{C}(5)$, and $\text{C}(6)$, exhibit large thermal displacements, generally with the largest dimension of the ellipsoid oriented parallel to a

TABLE IVA
BOND DISTANCES AND ANGLES:
DISTANCES (Å)^a

Bond	Distance	Bond	Distance
$\text{Cu}\text{—O}(1)$	1.973 (5)	$\text{C}(5)\text{—C}(6)$	1.371 (14)
$\text{Cu}\cdots\text{O}(2)^b$	2.415 (5)	$\text{C}(6)\text{—C}(7)$	1.381 (12)
$\text{Cu}\text{—N}(1)$	2.024 (7)	$\text{C}(7)\text{—C}(2)$	1.396 (11)
$\text{C}(1)\text{—O}(1)$	1.276 (8)	$\text{N}(1)\text{—H}(1)$	0.86 (9)
$\text{C}(1)\text{—O}(2)$	1.244 (8)	$\text{N}(1)\text{—H}(2)$	0.85 (10)
$\text{C}(1)\text{—C}(2)$	1.492 (10)	$\text{C}(4)\text{—H}(4)$	0.93 (9)
$\text{C}(2)\text{—C}(3)$	1.405 (10)	$\text{C}(5)\text{—H}(5)$	1.00 (9)
$\text{C}(3)\text{—N}(1)$	1.439 (10)	$\text{C}(6)\text{—H}(6)$	0.98 (9)
$\text{C}(3)\text{—C}(4)$	1.380 (11)	$\text{C}(7)\text{—H}(7)$	0.90 (10)
$\text{C}(4)\text{—C}(5)$	1.393 (12)		

^a Estimated standard deviations are given in parentheses and are calculated from those derived for the positional parameters.

^b The dotted line represents a bond between a copper atom and the carbonyl oxygen of a ligand attached to a different copper atom.

TABLE IVB
BOND DISTANCES AND ANGLES: ANGLES (DEGREES)^a

Bond	Angle	Bond	Angle
O(1)—Cu—N(1)	87.1 (2)	C(3)—C(4)—C(5)	119.9 (7)
O(1)—Cu···O(2) ^b	89.4 (2)	C(4)—C(5)—C(6)	119.7 (8)
O(2)···Cu—N(1)	93.8 (2)	C(5)—C(6)—C(7)	120.8 (9)
Cu—O(1)—C(1)	126.7 (4)	C(6)—C(7)—C(2)	120.7 (8)
O(1)—C(1)—O(2)	123.1 (7)	H(1)—N(1)—H(2)	121 (9)
O(1)—C(1)—C(2)	119.6 (6)	C(3)—C(4)—H(4)	123 (6)
O(2)—C(1)—C(2)	117.4 (6)	C(5)—C(4)—H(4)	117 (6)
C(1)—C(2)—C(3)	121.7 (6)	C(4)—C(5)—H(5)	120 (5)
C(1)—C(2)—C(7)	120.4 (7)	C(6)—C(5)—H(5)	120 (5)
C(3)—C(2)—C(7)	118.0 (7)	C(5)—C(6)—H(6)	124 (5)
C(2)—C(3)—N(1)	118.8 (6)	C(7)—C(6)—H(6)	115 (5)
C(4)—C(3)—N(1)	120.3 (7)	C(6)—C(7)—H(7)	123 (6)
C(2)—C(3)—C(4)	120.9 (9)	C(2)—C(7)—H(7)	116 (6)

^a Estimated standard deviations are given in parentheses and are calculated from those derived for the positional parameters.

^b The dotted line represents a bond between a copper atom and the carbonyl oxygen of a ligand attached to a different copper atom.

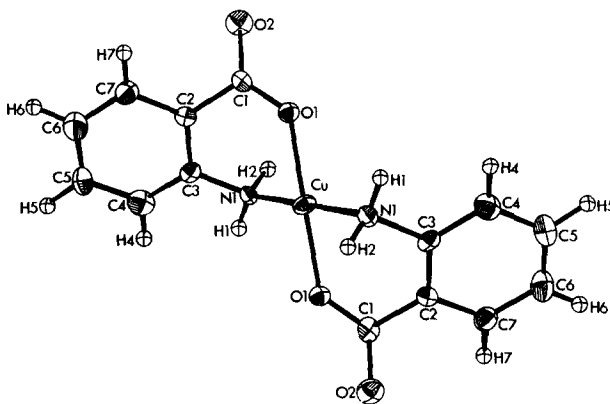


FIG. 4. Thermal ellipsoid drawing of $\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ as viewed along bc plane and 30° below $[010]$.

bond. As the number of bonds to an atom increases (bonds to hydrogen not included), the magnitude of the thermal vibration decreases and the ellipsoid becomes more spherical in shape. This effect is particularly pronounced for C(3) and C(2), each of which is bonded to three other atoms. On the other hand, O(2) exhibits extensive thermal motion in what appears to be a wagging mode. This large thermal displacement of the O(2) would seem to indicate that it is not that strongly

bonded to copper or, at any rate, not as strongly as are N(1) and O(1), whose thermal ellipsoids are markedly smaller. The thermal motion of the copper is clearly related to the nature of its coordination. The long axis of the thermal ellipsoid is directed towards the axially coordinated O(2) atoms, again a probable indication that the axial bonds are weaker than the equatorial bonds. The other two principal axes are much shorter and nearly equal in length, and they lie in the plane defined

by the four equatorially coordinated atoms. However, unlike the case with the long axis, the shorter axes are directed between rather than along the bonds.

$\text{Cu}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$ is one of a rare group of copper-amino acid complexes where both oxygens of the carboxylate group are active in bonding (14). Other examples include copper (II) glutamate dihydrate (15), glycylglycylglycinato-copper (II) chloride sesquihydrate (16), diammine(ortho-phthalato) copper (II) (17), copper gamma-aminobutyrate and the dihydrate (12).

However, bis(ortho-aminobenzoato)copper (II) is unique in that each carbonyl oxygen, O(2), comes from a different ligand.

The powder diffraction pattern of bis(ortho-aminobenzoato)zinc(II) is similar to, but not identical with, that of the copper complex. The diffraction patterns of the nickel and cobalt complexes with ortho-aminobenzoic acid are identical to that of the zinc complex, indicating that these three compounds are isostructural. Intuitively, one would surmise that the Zn-O(2) distance is shorter than the Cu-O(2) distance and that the Zn-O(2) distance has a magnitude of ca. 2.0 Å, thereby giving rise to undistorted octahedral coordination.

Acknowledgments

The National Research Council of Canada Crystallographic Programs (18) were used for most of the computational work. The full matrix least-squares refinement was performed using the ORXFLS3 program of Busing et al. (19). The thermal ellipsoid drawing was made using the program ORTEP-II of Johnson (20).

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