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Axial Bond Length Contraction in CuX_5 Complexes. The Structures of Hexaamminechromium(III) Pentabromocuprate(II) and Hexaamminechromium(III) Tribromodichlorocuprate(II)

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The crystal and molecular structure of hexaamminechromium(III) pentabromocuprate(II), $[Cr(NH_3)_6][CuBr_5]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $Fd3c$ of the cubic system with 32 formula units per unit cell with $a = 23.042$ (4) Å. The calculated density, 2.70 g/cm³, agrees closely with that of 2.69 g/cm³ measured by flotation. The structure has been refined by full matrix least-squares methods to a final weighted R factor on F of 3.1% for the 189 independent reflections with $F^2 > 3\sigma(F^2)$. The $Cr(NH_3)_6{}^{3+}$ ion is crystallographically required to have $\bar{3}(S_6)$ site symmetry; the N–Cr–N angle is 89.6 (2)° and the Cr–N bond length is 2.059 (6) Å. The $CuBr_5{}^{3-}$ anion is required crystallographically to have $32(D_3)$ site symmetry and is a regular trigonal bipyramid. The axial bond length is 2.4500 (22) Å and the equatorial is 2.5191 (17) Å, which is a difference of 0.0691 (26) Å. The geometry is compared in detail with that of the $CuCl_5{}^{3-}$ ion where this difference is 0.098 (23) Å. A simple force field model is described which quantitatively explains these geometries, based on the stereochemical activity of the metal d electrons and Born ligand–ligand repulsion forces. The structure also has been determined for a compound of composition $[Cr(NH_3)_6][CuBr_3Cl_2]$. This crystal is found to have random disorder of bromine and chlorine atoms between axial and equatorial positions.

Introduction

The structure determination of $[Cr(NH_3)_6][CuCl_5]$[1] provided the first unambiguous example of a trigonal-bipyramidal complex formed from equivalent monodentate ligands in which the axial bond length is significantly shorter than the equatorial. This contraction was explained as a manifestation of the stereochemical activity of the metal d electrons, caused by the nonspherical electron distribution of the open d shell. In particular, d^9 and low-spin d^8 or d^7 configurations are expected to give rise to a contraction in the axial bond lengths. The geometries of a number of subsequent structures have been explained using similar arguments[2-7] with only two marginal exceptions.[2,8] One of the expectations of this model is that larger ligands, for which ligand–ligand repulsion effects become more important, should tend to make the axial and equatorial bond lengths more nearly equal. To test this we have determined the structure of $[Cr(NH_3)_6][CuBr_5]$. We have also completed the structure analysis of a mixed salt, $[Cr(NH_3)_6][CuCl_2Br_3]$, whose preparation has been reported earlier.[9]

Experimental Section

$[Cr(NH_3)_6][CuBr_5]$. Preparation of Crystals.—Crystals of $[Cr(NH_3)_6][CuBr_5]$[10] were prepared by using a diffusion apparatus in which the reactant solutions were separated by a sintered-glass disk (Figure 1). In this preparation, one cavity contained 130 ml of 48% HBr, 30 g of NaBr, and 10 g of $CuSO_4 \cdot 5H_2O$. The second cavity contained 2 g of $[Cr(NH_3)_6]Br_3$ and 130 ml of 48% HBr. After a few days black crystals of $[Cr(NH_3)_6][CuBr_5]$ were collected and washed with methanol. *Anal* Calcd for $[Cr(NH_3)_6][CuBr_5]$: H, 2.9; N, 13.6; Br, 64.7. Found: H, 2.9; N, 13.5; Br, 64.0. The density measured by flotation in a $CHBr_3$–CCl_4 solution is 2.69 g/cm³.

Determination of the Unit Cell and Collection of Intensity Data.—A series of precession photographs (Mo Kα, Zr-filtered radiation) for a large crystal exhibited Laue symmetry $m3m$ and the systematic absences hkl, $h + k \neq 2n$; $k + l \neq 2n$; $0kl$, $k + l \neq 4n$; hhl, $l \neq 2n$. These absences are consistent only with space group $O_h{}^8$-$Fd3c$ and prove isomorphism with $[Cr(NH_3)_6][CuCl_5]$.

The single lattice constant and orientation angles were determined by least-squares refinement using the setting angles of 12 reflections carefully centered with a narrow vertical slit and monochromatic radiation from a highly oriented graphite crystal.[11] The lattice constant (λ(Mo Kα_1) 0.70926 Å) was found to be 23.042 (4) Å at 22°. For 32 formula units per unit cell the calculated density is 2.70 g/cm³, which agrees closely with the observed density of 2.69 g/cm³.

Intensities were collected in the θ–2θ scan mode as previously described.[12] The crystal was intentionally not oriented along a symmetry axis in order to minimize the effects of multiple diffraction.[13] The scan rate was 1°/min. The scan was from 0.6° below the Kα_1 peak to 0.6° above the Kα_2 peak. Backgrounds were counted for 10 sec at both ends of the scan. No filters were used. Attenuators were not needed since the small crystal had no reflections with count rates greater than 10,000 cps. An entire octant, h, k, l all positive, or six equivalent forms, was collected to a Bragg 2θ angle of 50°. From 50 to 85° only those reflections whose indices were multiples of 4 were collected, since only these reflections were above background at high angles. The width at half-height of an ω scan at high values of 2θ was found to be about 0.08° in each direction, which indicates a satisfactory mosaic spread. The crystal chosen for data collection was an octahedron capped on several vertices. A total of 5360 reflections were observed. These were reduced to values of F^2 by applying the Lorentz–polarization correction

$$\frac{1}{Lp} = \frac{2 \sin 2\theta}{(\cos^2 2\theta_m + \cos^2 2\theta)}$$

where θ_m is the Bragg angle for the monochromator. Standard deviations were computed according to the equation

$$\sigma(I) = \left[CT + 9 + \frac{1}{4}(t_c/t_b)^2(B_1 + B_2) + (pI)^2 \right]^{1/2}$$

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TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $[Cr(NH_3)_6][CuBr_5]$

Atom	Position	Site symmetry	x	y	z	β_{11}[a] or B[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	32c	S_6-$\bar{3}$	0	0	0	807 (19)	β_{11}	β_{11}	−40 (27)	β_{12}	β_{12}
Cu	32b	D_3-32	$^1/_4$	$^1/_4$	$^1/_4$	1262 (19)	β_{11}	β_{11}	−41 (24)	β_{12}	β_{12}
Br_{ax}	64e	C_3-3	0.18861 (3)	x	x	1385 (12)	β_{11}	β_{11}	−111 (14)	β_{12}	β_{12}
Br_{eq}	96g	C_2-2	$^1/_4$	0.07731 (4)	$-y$	5425 (59)	1086 (18)	β_{22}	625 (24)	β_{12}	164 (20)
N	192h	C_1-1	0.06938 (27)	0.04834 (24)	−0.02892 (22)	866 (134)	1366 (167)	1479 (139)	−280 (119)	209 (102)	91 (108)
H_1			0.0578[d]	0.0852	−0.0345	3.9 (12)[c]					
H_2			0.0822	0.0332	−0.0626						
H_3			0.0978	0.0472	−0.0021						

[a] Multiplied by 10^6. The form of the thermal ellipsoid is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. [b] Isotropic temperature factor in square ångströms. [c] Hydrogens refined as a rigid group with the origin at the nitrogen coordinates and the group threefold axis coincident with the Cr–N bond. [d] Group angles, in radians: $\phi = 2.178$; $\theta = 2.810$; $\rho = -0.041$ (50).

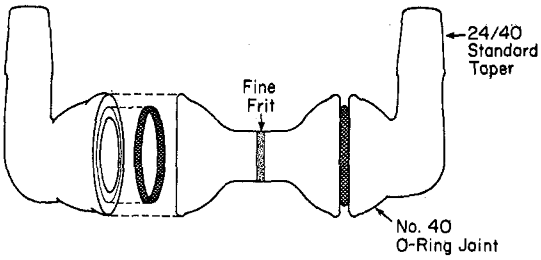

Figure 1.—Diffusion apparatus used for crystallization of nearly insoluble salts.

where CT is the total integrated count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in the time t_b, and $I = CT + 4.5 - 0.5(t_c/t_b)(B_1 + B_2 + 9)$. The appearance of the constants 4.5 and 9 is due to the effect of dropping the last decimal place when recording the total count in our scaler.[12] A value of 0.04 was assigned to the parameter p as a lower bound for the standard deviation. No drop was observed in the intensities of three standards which were monitored at regular intervals.

The dimensions of the crystal were determined with the aid of a micrometer eyepiece attached to a polarizing microscope. An absorption correction was then applied.[14] For a linear absorption coefficient of 160.5 cm^{-1} the transmission factors ranged from 2.62 to 3.90. The data were then averaged. Before correcting for absorption, the value of the weighted R factor was 6.6%. After averaging this dropped to 4.5%, indicating a significant improvement. A total of 775 independent reflections resulted from averaging of which 306 gave $F^2 > \sigma(F^2)$. The standard deviation of the average, $\sigma(F^2)$, was chosen as the maximum of that estimated from the range or by averaging individual standard deviations. The latter reflections were described as being above background and were used in the final refinement of the structure.

Refinement of the Structure.—Refinement of the structure was carried out by full-matrix least-squares techniques. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated magnitudes of the structure amplitudes, and the weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors used were those tabulated by Cromer and Mann[15] for Br, N, Cu, and Cr, and those of Stewart, *et al.*,[16] for H. The effects of both real and imaginary anomalous dispersion were included in the calculated structure factors.[17] The values of $\Delta f'$ and $\Delta f''$ for Cu, Cr, and Br were those given by Cromer.[18]

Trial parameters were the fractional coordinates and temperature factors for the chloro salt.[1] Anisotropic refinement on the nonhydrogen atoms gave values of unweighted and weighted R factors of 3.5 and 4.5%, where $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ and $R_2 = [(\Sigma w(|F_o| - |F_c|)^2)/\Sigma w(F_o)^2]^{1/2}$. A difference Fourier map did not clearly show any hydrogens although several possible peaks were present. The three independent hydrogens were introduced as a rigid group about the nitrogen with a N–H bond of 0.9 Å and a Cr–N–H angle of 109°. The nitrogen-hydrogen bond was assigned this short value in order to allow for the fact that the electron density of the hydrogen is polarized toward the nitrogen. The group was allowed to rotate about the Cr–N vector and converged to R_1 of 2.9% and R_2 of 3.1%. This indicates a significant improvement in the model since only two variables were added: one group angle and one group temperature factor. Scattering factors for charged atoms did not significantly improve the refinement. The possibility of freely rotating hydrogens was considered; however, the strong preference of the group for one particular orientation is convincing evidence that the hydrogens are localized. Free rotation may be hindered by the formation of weak hydrogen bonds to the bromine atoms and by crystal packing forces. The final error in the observation of unit weight, defined as

$$\left(\frac{\sum(|F_o| - |F_c|)^2/\sigma^2(F_o)}{N_o - N_v}\right)^{1/2}$$

is 0.64, where N_o and N_v are the number of observations and variables, respectively. This value indicates that the parameter p is somewhat too large. This does not affect the magnitude of the atom parameters or their standard deviations. There is no uniform trend in the agreement as a function of the magnitude of F. The final value of R_2 for the 306 reflections with $F^2 > \sigma(F^2)$ is 6.3%. For the 189 reflections with $F^2 > 3\sigma(F^2)$, R_2 is 3.1%.

The final values of the atomic parameters and their standard deviations as estimated from the inverse matrix and the error in the cell constant are given in Table I. Table II lists important distances and angles that may be derived from these parameters.[19] Table III lists rms amplitudes of vibration along the principal axes of the thermal ellipsoids.

TABLE II

CALCULATED BOND LENGTHS AND ANGLES AND SELECTED NONBONDED DISTANCES

Bond	Distance, Å	Atoms	Angle, deg
Cu–Br_{ax}	2.4500 (22)	N–Cr–N	89.64 (20)
Cu–Br_{eq}	2.5191 (17)		
Difference	0.0691 (26)		
Cr–N	2.059 (6)	Br_{eq} (1st principal axis and eq plane)	9.6 (8)
	Nonbonded Interactions		
Br_{eq}–H_1	2.60	Br_{eq}–H_1–N	159.1
Br_{eq}–H_2	2.65	Br_{eq}–H_2–N	157.3
Br_{ax}–H_3	2.58	Br_{ax}–H_3–N	167.7
Br_{eq}–Br_{ax}	3.51		
Br_{eq}–Br_{eq}	4.36		
Br_{eq}–N	3.46		
Br_{ax}–N	3.46		

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(14) In addition to various local programs for the CDC 6400 computer, local modifications of the following programs were employed: Hamilton's GONO9 absorption program, Zalkin's FORDAP Fourier and Patterson Program, Ibers' NUCLS least-squares program based on Busing and Levy's ORFLS, Busing and Levy's ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.

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(19) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III
ROOT-MEAN-SQUARE AMPLITUDES (Å) OF VIBRATION ALONG PRINCIPAL AXES

Atom	Axis 1	Axis 2	Axis 3
Cu	0.178 (5)	0.188 (3)	0.188 (3)
Cr	0.138 (8)	0.151 (4)	0.151 (4)
Br_{eq}	0.152 (3)	0.180 (3)	0.386 (3)
Br_{ax}	0.176 (3)	0.201 (2)	0.201 (2)
N	0.133 (17)	0.194 (18)	0.205 (13)

$[Cr(NH_3)_6][CuBr_3Cl_2]$.—Dark red crystals of the compound were obtained from W. Callins of this department. The crystals were all octahedra or octahedral fragments. A series of precession and Weissenberg photographs confirmed the space group O_h^8-*Fd3c*. The presence of the *c* glide was confirmed from diffractometer intensity measurements. The single lattice parameter was taken from a least-squares refinement of the setting angles of 28 reflections which had been carefully centered on a General Electric card-controlled XRD diffractometer. With the use of unfiltered radiation (λ(Mo $K\alpha_1$) 0.70926 Å) the lattice parameter was found to be 22.644 (4) Å at 21°. For 32 formula units in the unit cell the calculated density is 2.42 g/cm^3 which agrees closely with the observed density of 2.45 g/cm^3 obtained by flotation in $CHBr_3$ and CCl_4. The preliminary conclusion that the structure is ordered[9] is incorrect and due to the incorrect assignment of occupation factors to the chlorines and bromines. They are in fact randomly scrambled to within the precision of this experiment. We have subsequently prepared a number of other salts containing anions of the stoichiometry $CuBr_xCl_{5-x}{}^{3-}$ where *x* is in general nonintegral and appears to be continuously variable. All of these salts appear to exhibit *Fd3c* space group symmetry and disorder of the halides.

For the final refinement, scattering factors for an atom which was three-fifths bromine and two-fifths chlorine were interpolated from the scattering factors of the individual atoms. The positions of one axial and one equatorial "weighted" atom were refined with initial values of the positional parameters those of the $CuBr_5{}^{3-}$ salt. The refinement, which included no contribution from hydrogen atoms, gave a weighted *R* factor of 9.7%. Refinement of the occupation factor for axial and equatorial coordination sites indicated that the complex is completely disordered. The complex, although disordered, is trigonal bipyramidal but the uncertainty in its geometry introduced by the disorder precludes further discussion.

Description of the Structure of $[Cr(NH_3)_6][CuBr_5]$

The salt consists of discrete $Cr(NH_3)_6{}^{3+}$ and $CuBr_5{}^{3-}$ ions. The $CuBr_5{}^{3-}$ moiety is a regular trigonal bipyramid (Figure 2). The axial bond length of 2.4500 (22) Å is significantly shorter (27 standard deviations) than the equatorial bond length of 2.5191 (17) Å. The difference is 0.0691 (26) Å, which is significantly less than the axial–equatorial difference of 0.0948 (23) Å observed for $CuCl_5{}^{3-}$.[1] The standard deviations given here correctly account for the effect of covariance in the calculations. The thermal ellipsoids of the chloro and bromo anions differ somewhat, although the site symmetry is the same. The axial bromine is only slightly anisotropic. The rms amplitudes of vibration are slightly larger than for the chloro complex. The equatorial bromine is very anisotropic; the amplitude of vibration along the Cu–Br_{eq} bond is 0.152 (3) Å, and the amplitude along the principal axis normal to this bond and with largest projection in the Cu–Br_{ax} direction is 0.180 (3) Å. However, the amplitude of the vibration along the principal axis which is nearly in the equatorial plane and is normal to the Cu–Br_{eq} bond is much larger, 0.386 (3) Å. The angle between this ellipsoid axis and the equatorial plane is 9.6 (8)°, much smaller than the analogous chlorine angle of 20.8 (3)°.

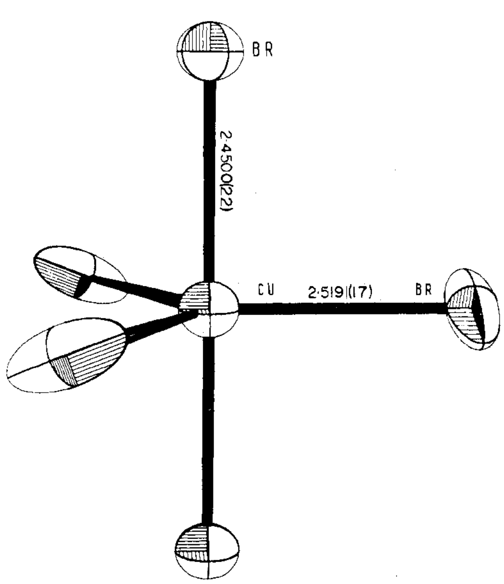

Figure 2.—A perspective drawing of $CuBr_5{}^{3-}$. The thermal ellipsoids represent 50% probability contours.

The axial and equatorial Cu–Br bond lengths corrected for the effects of thermal motion are as follows:[20] riding model, 2.452 (2), 2.542 (2) Å; independent model, 2.481 (2), 2.548 (2) Å. The three differences follow: uncorrected, 0.069 (3) Å; riding, 0.089 (3) Å; independent, 0.087 (3) Å. All of these are significantly less than the corresponding differences for $CuCl_5{}^{3-}$.

The $Cr(NH_3)_6{}^{3+}$ cation is essentially the same as in the chloro complex. The N–Cr–N angle agrees to within 0.01°, which is far less than one standard deviation. The Cr–N bond lengths of 2.064 (3) Å for the chloro complex and 2.059 (6) Å for the bromo complex agree very closely. The hydrogens, refined here as a group, are positioned similarly to the independently refined hydrogens in the chloro complex. Any hydrogen bonds are weak since the N–H · · · Br interactions are about the same as the sum of the van der Waals radii. The shortest Br–N distances are 3.4–3.5 Å; the N–H–Br angles are near 160°.

Structural Model

We can quantitatively express the structural effects of ligand–ligand repulsion in the following way. Assume a potential field for the $CuX_5{}^{3-}$ ion which is electrostatic for the attractive part but which expresses the repulsive part by the Born model. If r_1 is the Cu–X axial bond length and r_2 the equatorial, we can write the potential energy per complex, *U*, as

$$U = A_e + R_e + A_p + R_{m_1} + R_{m_2} + R_l$$

where

$$R_{m_1} = 2B_{m_1}[\exp(-r_1/\rho)]$$

$$B_{m_1} = b[\exp((r^+{}_1 + r^-)/\rho)]$$

$$R_{m_2} = 3B_{m_2}[\exp(-r_2/\rho)]$$

$$B_{m_2} = b[\exp((r^+{}_2 + r^-)/\rho)]$$

$$R_l = 6B_l \exp(-r_{12}/\rho) + 3B_l \exp(-r_{22}/\rho) + B_l \exp(-r_{11}/\rho)$$

$$B_l = b[\exp(2r^-/\rho)]$$

The term A_e is the purely electrostatic attraction between the copper ion (assumed charge 2+) and the ha-

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(20) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

lide (1−). The term R_e is the electrostatic ligand–ligand repulsion. The term A_p is the attraction term caused by the interaction of the central cation charge with the induced dipole of the halide. The assumed polarizabilities were 2.98 and 4.24 Å^3 for Cl and Br, respectively. The other variables are defined as follows; ρ is a softness parameter (discussed later), b is the single repulsion parameter and is variable, r^{+}_{1} is the ionic radius of the Cu^{2+} ion in the axial direction, r^{+}_{2} is the Cu^{2+} ionic radius in the equatorial direction, r^{-} is the halide radius, r_{12} is the axial–equatorial distance $(\sqrt{r_1^2 + r_2^2})$, r_{22} is the equatorial–equatorial distance $(\sqrt{3}r_2)$, and r_{11} is the axial–axial distance $(2r_1)$. The softness parameter, ρ, has been found to be approximately constant for all of the alkali halides.[21,22] We have used an average value of those found previously, 0.339 Å. Ionic radii of the Huggins-Mayer form[22] were chosen. These were 1.65 for Cl^-, 1.90 for Br^-, and 0.86 Å for Cu^{2+} (axial, r^{+}_{1}). The value for r^{+}_{2} was chosen as $r^{+}_{1} + \Delta r$, where Δr is the difference in the axial and equatorial ionic radii. It is this number that we wish to determine. It will be seen that there are now only two variable parameters: b and Δr. We have the equilibrium requirement that $\partial U/\partial r_i = 0$. This gives a total of four observations, two each for $CuCl_5^{3-}$ and $CuBr_5^{3-}$. A nonlinear least-squares refinement can now be carried out, minimizing the function

$$R = \sum_i \left(\frac{\partial U}{\partial r_i}\right)^2$$

We have used for this refinement the full-matrix least-squares program ORGLS.[23] Derivatives were determined numerically, and iteration was performed until convergence. The resultant Δr is 0.12 (1) Å for $b = 0.026$. *Therefore, in the absence of any ligand–ligand repulsion effects the axial bond lengths would be expected to be 0.12 Å shorter than the equatorial.*

Discussion

The difference in axial and equatorial bond lengths in $CuBr_5^{3-}$, 0.0691 (26) Å, as compared with $CuCl_5^{3-}$, 0.0948 (23) Å, confirms the trend predicted earlier.[1] It can be expressed adequately on a quantitative basis by a simple force field calculation which explicitly includes the ligand–ligand repulsion and anisotropy in the effective ionic radius of the copper ion in a trigonal-bypyramidal environment. The geometry observed for $CuBr_5^{3-}$ contradicts that predicted by Allen and El-Sharkawy[24] to explain the apparent anomaly that the ligand field splitting for $CuBr_5^{3-}$ is greater than that for $CuCl_5^{3-}$. The values of Δ_1 and Δ_2, as defined by Allen and Hush,[25] are Δ_1 = 906 and 945 cm^{-1} and Δ_2 = 932 and 986 cm^{-1} for $CuCl_5^{3-}$ and $CuBr_5^{3-}$, respectively. This is probably best explained by the introduction of covalent terms in the ligand field calculations as explicitly considered by Smith.[26]

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The Crystal and Molecular Structure of Bis(phenoxyacetato)triaquocopper(II), a Monomeric, Pentacoordinate Cupric Carboxylate Adduct

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A single-crystal X-ray structural analysis has shown bis(phenoxyacetato)triaquocopper(II) to be one of the very few known examples of a discrete and monomeric five-coordinate copper(II) complex in which a copper atom is bound to five monodentate ligands. This compound crystallizes in the triclinic space group $P\bar{1}$ with four formula units in a cell of dimensions a = 6.40 (1) Å, b = 9.28 (2) Å, c = 32.01 (6) Å, α = 100° 7′ (10′), β = 78° 50′ (10′), and γ = 90° 12′ (10′). Observed and calculated densities are 1.55 (2) and 1.518 g/cm^3, respectively. The structural determination was based upon 2185 visually estimated film data and a least-squares refinement which converged to a conventional R factor of 0.084. In the crystalline state, $Cu(O_2CCH_2OC_6H_5)_2(H_2O)_3$ exists as monomeric pentacoordinate molecules linked by hydrogen bonds into sheets perpendicular to the c axis. Essentially identical configurations are observed for the two crystallographically independent molecules. The copper atom is coordinated to two monodentate phenoxyacetate groups and three water molecules in a distorted square-pyramidal configuration, with Cu–O bonds ranging in length from 1.954 (16) to 2.280 (17) Å. Opposite the apical coordination site, the copper atom is involved in long contacts of *ca.* 2.96 Å to two uncoordinated carboxylate oxygen atoms.

Introduction

Magnetic susceptibility studies of a series of copper(II) carboxylate derivatives have been carried out by Hatfield, *et al.*,[1] in a study of the relationship between the tendency toward adoption of the binuclear cupric acetate structure for a particular carboxylate and the magnitude of the dissociation constant of the parent acid.[2,3] Among the compounds examined were hy-

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