Structure and Stability of Carboxylate Complexes. 20. Diaqua Bis(methoxyacetato) Complexes of Nickel(II), Copper(II), and Zinc(II): A Structural Study of the Dynamic Pseudo-Jahn−Teller Effect

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The crystal structure of *trans*-diaquabis(methoxyacetato)copper(II), $C_6H_{14}O_8Cu$, has been determined by neutron diffraction at 4.2 K (monoclinic, $P2_1/n$, $a = 6.88(1)$, $b = 7.19(1)$, $c = 9.77(2)$ Å, $\gamma = 95.7(1)°$, ($Z = 2$)) and by X-ray diffraction at 125, 165, 205, 240, 265, 295, and 325 K. These measurements show that there is no phase change in the temperature range 4.2−325 K. The copper(II) coordination at 4.2 K is a tetragonally distorted elongated rhombic octahedron (Cu−OOC 1.955(1), Cu−OMe 2.209(1), and Cu−OH_2 2.031(2) Å). As the temperature increases to 325 K, the Cu−OOC bonds shorten slightly to 1.934(5) Å, the Cu−OMe bonds shorten more markedly to 2.137(4) Å, and Cu−OH_2 lengthens to 2.155(6) Å to give a tetragonally distorted compressed rhombic octahedron. For comparison the structure of the isomorphous nickel(II) complex (monoclinic, $P2_1/n$, $a = 6.633(1)$, $b = 7.192(1)$, $c = 10.016(2)$ Å, $\gamma = 98.30(2)°$, ($Z = 2$)) has been redetermined at 295 K and the structure of the analogous zinc(II) complex (orthorhombic, $F2dd$, $a = 7.530(1)$, $b = 13.212(1)$, $c = 21.876(2)$ Å ($Z = 8$)) has also been determined. The nickel(II) complex has an almost regular *trans* (centrosymmetric) octahedral coordination (Ni−OOC 2.022(1), Ni−OMe 2.043(1), and Ni−OH_2 2.077(2) Å). However, zinc(II) has a very distorted octahedral coordination with the zinc atom on a 2-fold axis with the water molecules and the methoxy ligators *cis* and the carboxylate ligators *trans* (Zn−OOC 1.985(1), Zn−OMe 2.304(2), and Zn−OH_2 2.038(2) Å). The variation in the dimensions of the copper(II) coordination sphere is discussed in terms of static (low temperature) and planar dynamic (high temperature) pseudo-Jahn−Teller effects.

Introduction

Distorted stereochemistries are to be expected for Cu(II) complexes[1] as a consequence of the nonspherical symmetry of the d^9 electronic configuration. These are usually ascribed to the Jahn−Teller or pseudo-Jahn−Teller effect with associated vibronic coupling.[1−3] The vast majority of 6-coordinate Cu(II) complexes are static Jahn−Teller systems with tetragonally elongated coordination octahedra. The original and later treatments of the Jahn−Teller phenomenon were unable to rationalize the marked preponderance of the elongated distortion. However, a simple model is now available[2,4] based upon the more favorable stabilization accompanying $3d_{z^2}$-4s mixing when d_{z^2} is doubly occupied causing elongation in contrast to single occupation of d_{z^2} causing compression. Regular octahedral or trigonal Cu(II) complexes with six identical donor atoms are found occasionally and usually occur in crystals with high copper site symmetry. These are dynamic Jahn−Teller systems, visualized as having equal thermal populations of the three wells in the "warped Mexican hat" model for potential energy surfaces. The wells correspond to three tetragonally elongated octahedral species with orthogonal elongation axes. If all three wells are of equal energy and there is sufficient thermal energy, the wells will be equally occupied and diffraction experiments will show a pseudo-octahedral structure with all six copper ligand bond lengths equal. If two of the wells are of approximately equal energy, but the third of much higher energy, and essentially unoccupied, then two tetragonally elongated octahedra will be averaged and the structure observed by diffraction methods appears to be a compressed octahedron. These tetragonally compressed octahedral systems are also rare.[1,3]

A large number of *trans*-diaquabis(chelate)copper(II) complexes of 2-hydroxy, 2-alkoxy, and 2-aryloxy carboxylates have been shown[5] by X-ray diffraction studies to have elongated distorted octahedral structures at room temperature. The chromophore in these systems is $CuO_2O_2'O_2''$ with three different pairs of oxygen ligators, two of which are part of chelate rings. However, although there will be some site strain,[2,6,7] the bond lengths and angles are not significantly different from those found in other CuO_6 systems. The only exception was *trans*-diaquabis(methoxyacetato)copper(II), which we found[8] to have a compressed distorted octahedral structure at room temperature. Other examples of Cu(II) systems for which diffraction studies indicate compressed octahedral geometry include $Cu_3(OH)_2V_2O_7{\cdot}2H_2O$ (volborthite),[9] $KCu_3(OH)_2[(AsO_4)H(AsO_4)]$,[10] $KAlCuF_6$,[11] and $(3\text{-chloroanilinium})_8[CuCl_6]$-

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Table 1. Crystal Data and Experimental Parameters for the Neutron and X-ray Structure Analyses of the Copper, Nickel, and Zinc Diaquabis(methoxyacetato) Complexes

	diquabis(methoxyacetato)copper(II)								Ni(II)	Zn(II)
fw	277.72								272.86	279.56
T, K	4.2	125	165	205	240	265	295	325	295	295
cryst system	monoclinic								monoclinic	orthorhombic
a, Å	6.88(1)	6.900(2)	6.919(1)	6.923(2)	6.936(1)	6.944(2)	6.953(3)	6.972(2)	6.933(1)	7.530(1)
b, Å	7.19(1)	7.190(1)	7.206(1)	7.206(1)	7.217(1)	7.221(1)	7.228(2)	7.244(1)	7.192(1)	13.212(1)
c, Å	9.77(2)	9.874(2)	9.936(2)	9.983(1)	10.01(1)	10.072(1)	10.128(3)	10.166(1)	10.016(3)	21.876(2)
γ, deg	95.7(1)	95.70(1)	95.84(2)	95.95(1)	96.25(2)	96.34(1)	96.7(3)	96.80(1)	98.30(2)	
V, Å^3	480.9	487.4	492.8	495.3	498.1	501.9	505.5	509.9	494.2	2176.4
ρ_{calcd}, g cm^{-3}	1.918	1.892	1.871	1.862	1.851	1.837	1.825	1.809	1.834	1.706
space group	$P2_1/n$ (No. 14)								$P2_1/n$ (No. 14)	$F2dd$ (No. 43)
Z	2								2	8
radiation	neutrons	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Mo Kα
λ, Å	1.174	0.710 68	0.710 68	0.710 68	0.710 68	0.710 68	0.710 68	0.710 68	1,5418	0.710 68
no. obsd $I \geq 3\sigma(I)$	1101	2755	1404	626	904	605	1967	589	924	1579
μ, cm^{-1}	2.62	22.66	22.41	22.30	22.12	22.00	21.85	21.66	30.87	23.29
final R,[a] R_w,[b] %	3.8, 4.6	2.45, 2.79	3.76, 4.18	3.70, 4.09	3.41, 3.60	3.53, 4.06	3.374, 3.78	3.70, 4.90	2.37, 2.68	2.57, 3.25

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]\}^{1/2}$.

Cl_4.[12] The EPR spectra of (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$[13] and of diaquabis(methoxyacetato)copper(II)[6] have been reported for a range of temperatures. The latter measurements have been used as a basis for the prediction of the variation of the Cu−O bond lengths with temperature.

We now report a series of structural determinations of *trans*-diaquabis(methoxyacetato)copper(II) by single-crystal neutron diffraction at 4.2 K and XRD at a series of temperatures from 125 to 325 K, including a more precise redetermination of our structure at room temperature.[8] In addition, for comparison we have redetermined our earlier room-temperature structure of the Ni(II) analogue[14] and have determined the structure of the Zn(II) complex, also at room temperature.

For a variety of reasons the collection of the data and preparation of this paper have been protracted. A number of authors has quoted and discussed some preliminary values of our bond lengths[1,6,7] which were given at a conference.[15]

Experimental Section

Preparation. Nickel carbonate, basic copper carbonate, or zinc carbonate was dissolved in aqueous methoxyacetic acid. The excess of carbonate was filtered off from solutions (pH ≤ 5), which were left to crystallize. With care it was possible to grow tabular crystals of the nickel and zinc salts up to a maximum dimension of 5 mm and of the copper salt up to a maximum dimension of 20 mm.

Diffraction Analysis. For each structure determination, crystal data, some details of the measurement of the diffraction intensities, and the structure refinements are reported in Tables 1 and S1 (Supporting Information).

The neutron diffraction data for the Cu complex at 4.2 K were collected at the Institute Laue Langevin, Grenoble, France, using D15, a three-circle diffractometer of normal beam geometry and fitted with a helium "orange cryostat".[16] The crystals prepared for the neutron work were flattened parallelepipeds with large (110) and $(\bar{1}\bar{1}0)$ faces and smaller (101), $(\bar{1}01)$, $(10\bar{1})$, and $(\bar{1}0\bar{1})$ faces. The data were collected from two different crystals selected for their near cuboid habit. One crystal 1.9 × 1.9 × 1.5 mm was mounted about the [001] axis, and the second 1.3 × 1.3 × 1.57 mm was mounted about the [110] axis. D15 counted with both counter and crystal stationary. The observations, to which a polarization correction and an analytical absorption correction were applied, totaled 1449 from the [001] axis, which merged (R_m = 4.2%) to give 771 independent reflections and 719 from the [110] axis, which merged (R_m = 3.6) to give 577 independent reflections. The design of D15 gave unit cell parameters of significantly lower precision than the X-ray diffractometers. In the structure analysis the starting model was the X-ray structure at 125 K without hydrogen atoms. The hydrogen atoms were located by Fourier methods, and the model was refined by full-matrix least-squares analysis with anisotropic atomic displacement parameters for all atoms. Initially the data about the [001] and [110] axes were treated separately and their scale factors refined as two separate least squares parameters. Toward the end of the refinement the two data sets were merged to give 1101 unique reflections (R_m = 40%). At convergence $R = 0.038$ and $R_w = 0.046$ with unit weights.

For the X-ray structure analyses of the Cu complex, the data at 165 and 240 K were collected in Dr. A. M. Glazer's laboratory, Department of Physics, University of Oxford; the data at 205, 265, and 325 K were collected at the EPSRC X-ray Crystallography Service, Cardiff, Wales, by courtesy of Prof. M. B. Hursthouse; and the data at 125 and 295 K together with those for the Ni and Zn complexes were collected in our laboratory. Data reduction included Lorentz and polarization corrections. The structures of the Cu and Ni complexes had been solved previously[8,14] by Patterson heavy atom methods, and the present independent structure determinations used the same methods. Each starting model was generated individually from a given data set. The structure of the Zn complex was solved by direct methods (SIR92)[17] which yielded all non-hydrogen atom positions. Positional and first isotropic and then anisotropic displacement parameters for the non hydrogen atoms were refined to convergence by the least squares method minimizing $\Sigma\omega(F_o - F_c)^2$ for all observed reflections. The full normal matrix was used together with a Chebyshev polynomial weighting scheme[18] the parameters for which are given in Table S1. For all the structures an empirical absorption correction (DIFABS) was applied prior[19] to the final refinement cycles. Hydrogen atoms were included in the models at geometrically idealized positions, except in

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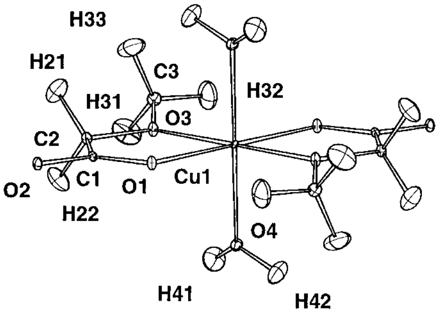

Figure 1. Molecular structure of *trans*-diaquabis(methoxyacetato)-copper(II) determined at 4.2 K by neutron diffraction showing 50% atomic displacement ellipsoids.

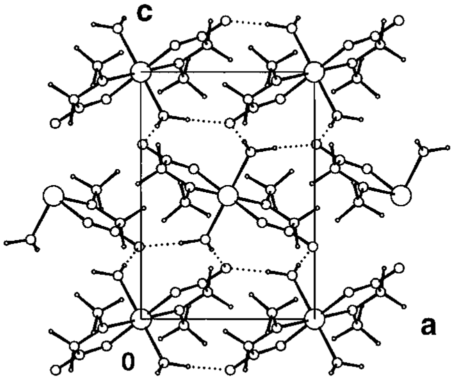

Figure 2. Crystal packing and H-bond network of diaquabis(methoxy-acetato)copper(II) from the neutron diffraction determination at 4.2 K, viewed along *b*.

the structure of the Cu complex at 125 K for which the space parameters and isotropic temperature factors of the hydrogen atoms were refined, and in the structure from neutron diffraction at 4.2 K for which the space parameters and anisotropic displacement parameters of the hydrogen atoms were refined. Final residuals are given in Table 1, and the atomic coordinates, in Table S2.

Except where indicated to the contrary, the Oxford CRYSTALS system was used[20] for all crystallographic calculations and CAMERON for crystallographic drawings.[21] Scattering factors were taken from Cromer and Waber.[22] The anisotropic displacement parameters are available as Supporting Information.

Results and Discussion

We have reported previously the crystal structures of the isostructural Ni and Cu complexes at room temperature.[8,14] The structural motif of the Ni and Cu species is a molecule of the centrosymmetric *trans*-diaquabis(methoxyacetato)metal(II) bis-chelate. These molecules are located at the inversion centers in the space group $P2_1/n$ and are connected by inter-molecular H-bonds between the pyramidal water molecules and carboxylate groups in neighboring molecules. The molecular structure is shown in Figure 1 together with the numbering scheme for the atoms and the crystal packing and H-bond network in Figure 2, each using the coordinates from the neutron diffraction determination at 4.2 K, and the bonded distances and interbond angles are given in Tables 2 and S3.

The structure of the zinc complex was determined for comparison. The structural motif of the zinc complex is a molecule of the noncentrosymmetric *cis*-diaquabis(methoxyacetato)zinc(II) shown in Figure 3 together with the numbering scheme for the atoms. The molecules are located on 2-fold axes in space group *F*2*dd*; see Figure 4. The zinc coordination sphere is much less regular than might be expected for a d^{10} center and even more distorted from regular octahedral geometry than that of the copper complex. The bonded distances and interbond angles are given in Table 2. The chelate rings are *cis* with short *trans* Zn−OOC bonds (1.985(1) Å) and longer *cis* Zn−OMe bonds (2.304(2) Å). The Zn−OH_2 bonds are short (2.038(2) Å) and *cis*, and the water oxygen atoms are pyramidal. Each water molecule forms two H bonds to the carboxylate oxygen atoms located outside the chelate rings of two neighboring complexes so that each complex forms four H bonds that together form a 3-dimensional H-bonded network. Some unconfirmed work mentioned by Hathaway[1b,23] is consistent with these bond lengths. A similar distorted octahedral zinc(II) coordination geometry with *cis* water ligands has been observed in the structures of the related compounds diaquabis(glycollato)-zinc(II)[24] and diaquabis(DL-lactato)zinc(II) hydrate.[25] The Zn−OH bonds in these compounds are markedly shorter than the Zn−OMe bonds in the methoxyacetato complex with the consequence that the distortions are less severe. However even in the ammonium Tutton's salt the $Zn(H_2O)_6^{2+}$ octahedron is distorted.[27] The *trans*-diaquazinc(II) isomers appear to be unknown.

The Ni(II) complex is isostructural with its Cu(II) analogue but with a much more regular octahedral coordination. The shortest Ni bond is Ni−OOC (2.022(1) Å) with a slight increase in the Ni−OMe bond (2.043(1) Å) and a further small increase in the Ni−OH_2 bond (2.077(1) Å). (In our earlier investigation of this compound[14] using Weissenberg photography, minor differences found in the bond lengths in the chelate rings were sufficient to suggest erroneously that the Ni−OMe bond was marginally shorter than the Ni−OOC bond.) The radial distortion parameter,[2] defined as $[\Sigma_i(r_i - \bar{r})^2]^{1/2}$, is very small, ≅0.05 Å, and suggests that site strains due to the presence of different ligator oxygens and to the fixed bite of the chelate rings are very small. Indeed the coordination sphere resembles that in the $Ni(H_2O)_6^{2+}$ ion in many salts[26] including the ammonium Tutton's salt.[27]

The structure of the Cu complex has been determined at 8 different temperatures from 4.2 to 325 K. The crystals decomposed at higher temperatures. The crystal structure is essentially the same at all temperatures, and there is no evidence for any phase change. The CuO_6 coordination polyhedron changes from an elongated rhombic octahedron with the long bonds to the *trans* ether oxygen atoms in the five-membered chelate rings at low temperature to a compressed rhombic octahedron with the short bonds to the *trans* carboxylate groups at high temperatures. Thus the principle axis rotates through 90°. The unit cell volume changed little between 4.2 and 125 K but increased smoothly by some 5% between 125 and 325 K. The increase in the unit cell volume largely reflects the increase in the length of the *c* axis which in turn reflects the increase in the Cu−OH_2 bond length; see Table 1 and Figure 5. The variation of bond lengths in the CuO_6 pseudo-octahedron is shown in Table 2 and Figure 6. The Cu−OOC bond, the most ionic of the Cu−O bonds, is the shortest of the three at

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Table 2. Interatomic Distances, Å, and Interbond Angles, deg, with Estimated Standard Deviations in Parentheses for the Diaquabis(methoxyacetato) Complexes

	diaquabis(methoxyacetato)copper(II)								Ni(II)	Zn(II)[a]
temp, K	4.2	125	165	205	240	265	295	325	295	295
M(1)−O(1)	1.955(1)	1.952(1)	1.955(2)	1.944(3)	1.948(2)	1.935(4)	1.933(1)	1.934(5)	2.022(1)	1.985(1)
M(1)−O(3)	2.209(1)	2.205(1)	2.195(2)	2.184(3)	2.174(2)	2.160(4)	2.144(1)	2.137(4)	2.043(1)	2.304(2)
M(1)−O(4)	2.031(2)	2.048(1)	2.064(2)	2.074(4)	2.099(3)	2.111(5)	2.139(2)	2.155(6)	2.077(1)	2.038(2)
mean M−O	2.065	2.068	2.071	2.067	2.074	2.069	2.072	2.075	2.047	2.109
O(1)···(3) (ligand bite)	2.626(2)	2.624(1)	2.626(3)	2.620(5)	2.629(3)	2.609(5)	2.612(2)	2.623(6)	2.606(2)	2.613(2)
O(1)−M(1)−O(3)	77.91(5)	78.03(2)	78.28(7)	78.6(1)	79.06(8)	78.9(1)	79.52(5)	80.1(2)	79.76(5)	74.65(7)
O(1)−M(1)−O(4)	89.09(7)	88.95(3)	88.94(9)	89.0(2)	89.0(1)	88.9(2)	88.61(6)	88.7(2)	88.79(6)	88.97(7)
O(3)−M(1)−O(4)	87.45(6)	87.55(3)	87.66(8)	88.0(2)	88.07(9)	88.3(2)	88.33(6)	88.3(2)	88.61(6)	103.63(7)

[a] Additional angles for Zn: O(1)−Zn(1)−O(1)^{I} 161.1(1), O(1)−Zn(1)−O(3)^{I} 91.47(7), O(1)−Zn(1)−O(4)^{I} 88.97(7), O(3)−Zn(1)−O(3)^{I} 86.41(1), O(3)−Zn(1)−O(4)^{I} 163.24(6), and O(4)−Zn(1)−O(4)^{I} 96.8(1) (I indicates equivalent position x, $^1/_2 - y$, $^1/_2 - z$).

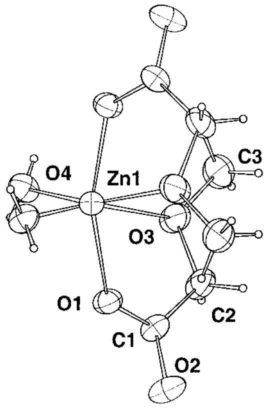

Figure 3. Molecular structure of *cis*-diaquabis(methoxyacetato)zinc(II) at 295 K showing 50% atomic displacement ellipsoids. The complex is noncentrosymmetric in space group *F*2*dd* with a crystallographic 2-fold axis along the bisector of the $H_2O-Zn-OH_2$ bond angle.

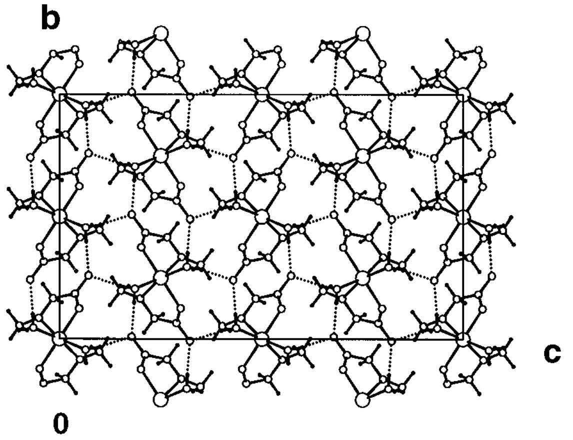

Figure 4. Crystal packing and H-bond network of *cis*-diaquabis(methoxyacetato)zinc(II) at 295 K viewed along *a*.

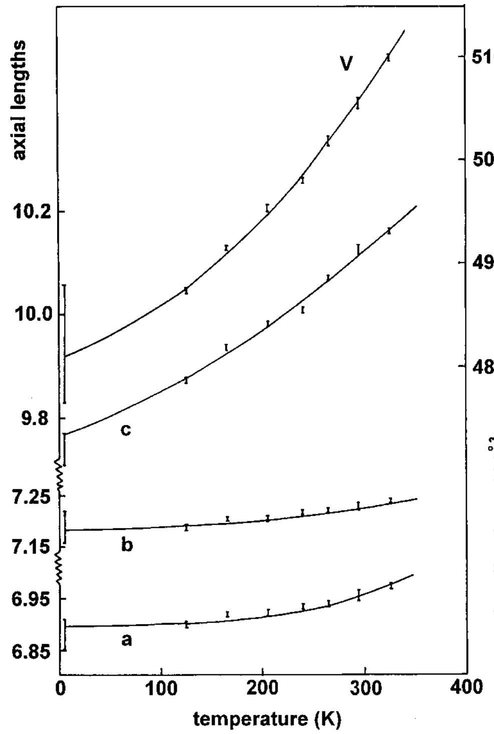

Figure 5. Axial lengths *a*, *b*, and *c* in Å (left-hand ordinate) and volume of the unit cell *V* in Å^3 (right-hand ordinate) for diaquabis(methoxyacetato)copper(II) plotted as a function of temperature.

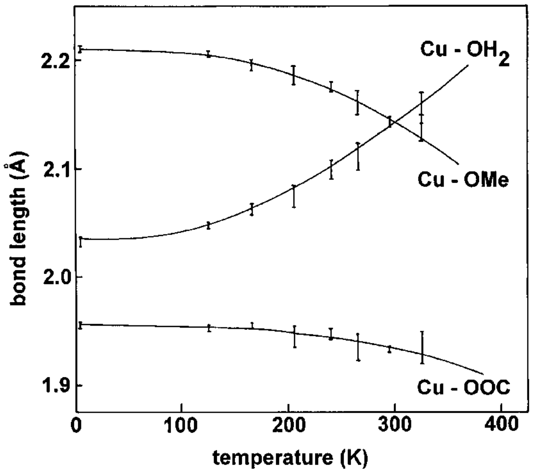

Figure 6. Variation of bond lengths in the CuO_6 pseudo-octahedron for diaquabis(methoxyacetato)copper(II) as a function of temperature.

all temperatures and shows a slight but probably significant contraction of about 1% with increasing temperature. By contrast, the average Cu−O bond length in the static α-[Cu(OOCH)$_2$] increases by about 1% over the same temperature range.[28] The Cu−OH$_2$ bond in the methoxyacetate lengthens by nearly 6% as the temperature increases from 4.2 to 325 K at which temperature it is the longest Cu−O bond. At 4.2 K the bond length is within the range of values found for "short" copper−water bonds but at 325 K the bond is shorter than expected for a "long" copper−water bond.[29] The Cu−OMe bond length decreases by some 3% as the temperature increases above 4.2 K and is marginally shorter than the Cu−OH$_2$ bond at 325 K. At ∼303 K the Cu−OH$_2$ and Cu−OMe bonds are equal in length; see Figure 6. The average Cu−O bond length

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of ~2.07 Å over this temperature range is slightly lower than in the analogous compounds studied previously at room temperature.[5] It increases by less than 0.5% over the temperature range, with the increase in the Cu−OH_2 bond length compensating for the decrease in the Cu−OMe bond length within the chelate rings. However the radial distortion parameter decreases by some 8% between 4.2 K and 325 K. The ligand bite of the methoxyacetato group decreases by less than 0.5%, and thus remains essentially constant at 2.62 Å.

The Cu(II) complexes are subject to some orthorhombic and tetragonal strain.[6,7] The molecules are only weakly linked together by intermolecular H bonds between the aqua ligands and carboxylate groups in neighboring molecules[8] (Figure 2 and Table S3) so that the copper centers are largely cushioned from interactions by their organic ligands. As judged[2,3] by the absence both of changes in the symmetry of the environment of the Cu(II) centers and also of structural phase transitions, there do not appear to be appreciable cooperative psuedo-Jahn−Teller effects. Following early studies[30] of the EPR spectra of the Cu compound at room temperature, Jakob and Reinen[6] made a detailed study of the variable-temperature EPR spectra which shows that the relative values of the molecular *g*-tensors are consistent with a $d_{x^2-y^2}$ ground state at low temperatures and a d_{z^2} ground state at ambient temperature. Further, using our preliminary Cu−O bond lengths at 295 and 125 K together with single-crystal and powder EPR data over the temperature range 4.2−350 K, they predicted the variation of bond length with temperature for the Cu−OH_2 and Cu−OMe bonds. Their model assumes that there is an ordered crystal structure at low temperatures with all the complexes in an elongated tetragonally distorted ground-state with the long bonds to the methoxy groups, state A, that dynamic disorder (fluxionality) occurs at higher temperatures with up to 50% occupancy of an elongated tetragonally distorted thermally accessible excited-state with the long bonds to the water molecules, state B, and that there is an elongated tetragonally distorted thermally inaccessible excited-state with the long bonds to the carboxylate oxygens. Below about 125 K only the ground-state is occupied and there is a static Jahn−Teller distortion. As the temperature is increased above 125 K occupancy of the thermally accessible excited-state increases and the predicted bond lengths are the weighted averages of the ground-state and excited-state dimensions. This behavior they named a "planar dynamic" Jahn−Teller distortion. Their predicted variation of bond lengths with temperature agrees remarkably well with the experimental trends we now report in Table 2 and Figure 6. Crucially Jakob and Reinen predicted a crossover of the Cu−OH_2 and Cu−OMe bond lengths at 283 K with the Cu−OH_2 bond shorter at the lowest temperatures and longer at the highest temperatures. Our experimental results confirm the crossover but at the somewhat higher temperature of 303 K. Above the crossover point the occupancy of state B must exceed that of state A. The implication is that with change of environment, as the crystal expands particularly in the *c* direction, the energy of state B must fall below that of state A. There is some evidence that small changes in environment in crystals lead to changes in the direction of the distortion in CuO_6 complexes. For example in the isomorphous copper Tutton salts, the direction of the distortion of the $Cu(OH_2)_6$ octahedron with reference to the crystal axes is different[31] in $K_2Cu(SO_4)_2{\cdot}6H_2O$ and $K_2Cu(SeO_4)_2{\cdot}6H_2O$. In the former, the direction of the distortion is the same as in the Rb, Cs, Tl, and the deuterated ammonium sulfate salts,[32] whereas in the latter it is the same as in the hydrogenous ammonium sulfate salt. Further, it has been reported[32] that the tetragonality of the deuterated ammonium sulfate salt varies with temperature but not to such a degree that a compressed octahedron is observed.

In the methoxyacetate complex it may be that the structure is ordered at all temperatures and that there are genuine changes in bond length, or it may be that at very low temperatures the complexes are ordered with Cu−OMe the elongated direction and that at higher temperatures there is a static disorder (on the X-ray time scale) with Cu−OMe the elongated direction on some sites and with Cu−OH_2 the elongated direction at the rest of the sites. At the temperature at which the Cu−OMe bond is equal in length to the Cu−OH_2 bond there must be 50% of each form. Above this temperature, when the Cu−OH_2 bond becomes longer than the Cu−OMe bond, a partial ordering must have taken place. It is unusual but not unprecedented for a crystal structure to pass continuously from an ordered to disordered state on heating and for this to be reversed on cooling, but even rarer for a range of disorder to be followed by further partial ordering at higher temperatures.

Further evidence for fluxionality in the CuO_6 coordination octahedron may be obtained from the atomic displacement parameters (adps),[33] values of which are given in Table S2. A problem in the interpretation of adps is one of time scale. The adp ellipsoid may represent the amplitude and direction of a molecular libration or vibration, a distribution over two or more positions in a static disorder, or some intermediate situation where the dynamics of the system are slow on the molecular time scale. For a static disordered or a dynamic Jahn−Teller system the principle axes of the adps would be expected to lie along the bond vectors.[33] The Ni complex is not subject to Jahn−Teller distortion, but nevertheless it is isostructural with its Cu analogue. Comparison of the direction cosines of the Ni−OOC, Ni−OMe, and Ni−OH_2 bonds with those of the principle axes of the adps shows that, as expected for a non-Jahn−Teller ion,[33] the major axes of the adp ellipsoids do not necessarily lie along the bond vectors. A similar comparison for the Cu complex shows that the principle axes of the adp ellipsoids also do not lie along the bond direction.

TLS (translation, libration, and screw motion) analyses[34] for the Ni complex and for the variable-temperature measurements for the Cu complex demonstrate that, although in both systems the motion of the whole molecule is not consistent with libration as a rigid body, the motion of the methoxyacetato ligand is consistent with rigid body behavior. However the principle motion of the methoxyacetato ligand in the nickel complex and in the copper complex at all temperatures is a libration (rotational oscillation) about an axis through its center of gravity and roughly parallel to the C(1)−C(2) bond and is therefore a bending of the ligand plane with respect to the O(1), Cu(1), O(3) plane. This motion is consistent with the likelihood that, for nondynamic systems, the bending modes are of greater amplitude than the stretching modes, that higher rms displacements will occur perpendicular to the metal−ligand bond directions, and that for dynamic systems the highest rms displacements might be expected to be along the bonds. In our system the predominance of bending motions over the inplane

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Table 3. Values of $\Delta U^{1/2}$ for the Metal-Oxygen Bonds in the Diaquabis(methoxyacetato)metal(II)[a]

	diaquabis(methoxyacetato)copper(II)								Ni(II)	Zn(II)
temp, K	4.2	120	165	205	240	265	295	325	295	295
$\Delta U^{1/2}$ (M ↔ 01), Å	0.036	0.047	0.042	0.071	0.056	0.045	0.064	0.042	0.060	0.046
$\Delta U^{1/2}$ (M ↔ 03), Å	0.051	0.048	0.046	0.043	0.082	0.090	0.093	0.086	0.037	0.056
$\Delta U^{1/2}$ (M ↔ 04), Å	0.048	0.045	0.035	0.046	0.094	0.090	0.098	0.085	0.018	0.022

[a] ΔU is defined as the difference between the component of the metal $\mathbf{U}_{ij}$ tensor in the direction of the metal−oxygen bond and the component of the oxygen $\mathbf{U}_{ij}$ tensor in the direction of the oxygen−metal bond.

bond stretching motions of the planar dynamic Jahn−Teller effect may be interpreted as due to the rather small changes in metal−ligand bond distance rather than as evidence for a static but variable distortion.

Indications of fluxionality can alternatively be obtained[33] from the adps by an examination of $\Delta U^{1/2}$, where ΔU is defined as the difference between the component of the metal $\mathbf{U}_{ij}$ tensor in the direction of the oxygen ligator and the component of the oxygen $\mathbf{U}_{ij}$ tensor in the direction of the metal center. It is usually considered that values of $\Delta U^{1/2}$ in excess of about 0.1 Å indicate fluxionality in CuO_6 systems. The values of $\Delta U^{1/2}$ in the directions of the Cu−OMe and Cu−OH_2 bonds, given in Table 3, are well below 0.1 Å at low temperatures, approach 0.1 Å at 240 K and above, and are greater than those in the direction of the Cu−OOC bond at most temperatures. These values indicate a static system at low temperature and fluxionality in the plane containing the Cu−OMe and Cu−OH_2 bonds above 240 K. Hathaway[1a] has previously made a similar suggestion based on values of $\Delta U^{1/2}$ obtained from preliminary data at 125 and 298 K. For the Ni and Zn complexes, which must be presumed to have static coordination spheres, all values of $\Delta U^{1/2}$ are substantially less than 0.1 Å, but greater in the M−OOC and M−OMe directions than in the M−OH_2 direction.

A recent detailed variable-temperature X-ray diffraction study of a another compressed octahedral Cu(II) system is the work[12] on (3-chloroanilinium)$_8$[$CuCl_6$]Cl_4. EXAFS measurements[35] and variable-temperature EPR measurements have also been reported.[13] The EXAFS studies indicate that the $CuCl_6^{4-}$ anion is an elongated octahedron at 10 K, whereas the variable-temperature X-ray diffraction measurements,[12c] if naively interpreted, indicate compressed octahedral coordination with almost invariant Cu−Cl bond lengths over the temperature range 156−296 K. However, EPR spectra suggest that above 55 K the $CuCl_6^{4-}$ polyhedra in doped samples[36] and in the pure compound are in dynamic exchange faster than the EPR time scale leading to a dynamically averaged Jahn−Teller distortion with an apparent compressed octahedral geometry. These results may be reconciled[12c] by an X-ray diffraction model with a 2-fold-disordered elongated rhombic octahedral coordination: this also explains the elongation of the adp ellipsoids of four of the six chlorine atoms in the direction of the Cu−Cl bonds. These measurements contrast with our results for the methoxyacetate complex in that (a) the adps for the $CuCl_6^{4-}$ anion give a clear indication of disorder or dynamic exchange but ours do not; (b) there is no significant variation of metal ligand bond lengths with temperature in $CuCl_6^{4-}$ even on the assumption that there is no disorder, whereas there is a variation in metal−ligand bond lengths in the methoxyacetate; (c) the temperature at which the disorder is frozen out is much lower for the $CuCl_6^{4-}$ than for the methoxyacetate (55 K contrasted with about 125 K); and (d) there is no indication that an elongated octahedron might be preferred for $CuCl_6^{4-}$ at higher temperatures. The most likely reasons for the differing behaviors of the two systems is that in $CuCl_6^{4-}$ there are six ligands which are identical except for their crystal environments whereas in the methoxyacetate there are three pairs of chemically distinct oxygen ligators.

Conclusion

The variable-temperature diffraction studies of *trans*-diaquabis(methoxyacetato)copper(II) offer no unequivocal evidence from the space coordinates or adps that there is static disorder. On the contrary, the results appear to be consistent with an ordered structure at all temperatures. The copper(II) complex shows a variation of bond length within the copper coordination sphere which, when considered with the anisotropic displacement parameters of the ligand atoms and the evidence from published EPR studies, is best described as a static system below 125 K and as a planar dynamic Jahn−Teller system at higher temperatures as suggested by Hathaway[1a] and Jacob and Reinen.[6]

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Supporting Information Available: Tables of structure determination parameters (Table S1), space parameters and anisotropic displacement parameters (Table S2), H atom positions (Table S2), and bond distances and bond angles (Table S3) for diaquabis(methoxyacetato)nickel(II), diaquabis(methoxyacetato)copper(II) at eight temperatures, and diaquabis(methoxyacetato)zinc(II) (15 pages). Ordering information is given on any current masthead page.

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