This fact implies that processes of deprotonation and ring closure of Hipt in the complexation would not be rate-determining. If such processes as deprotonation and/or ring closure are rate-limiting, values of activation parameters are expected to be almost the same regardless of the kind of metal ions. But this is not the case. Therefore, the reaction of the M^{3+} ion with the entering ligand (Hipt) is represented by eq 3, where K_{os} is the formation

$$M^{3+} + \text{Hipt} \overset{K_{os}}{\rightleftharpoons} M^{3+}\cdots\text{Hipt} \xrightarrow{k^*} M(\text{ipt})^{2+} + H^+ \qquad (3)$$

constant of the outer-sphere complex ($M^{3+}\cdots$Hipt). Interchange of one of coordinated solvents with an entering ligand on the outer-sphere complex should be the rate-limiting step. Thus, the observed second-order rate constant k is given by the product of K_{os} and the first-order rate constant k^* ($K_{os}k^*$), and then the observed volume of activation $\Delta V^\ddagger$ is given as the sum of ΔV_{os}° and $\Delta V^{*\ddagger}$, which are the volume change for the first step and the activation volume for the second step, respectively. Usually, $\Delta V^{*\ddagger}$ is split into two terms, $\Delta V^{*\ddagger}_{intr}$ and $\Delta V^{*\ddagger}_{solv}$. $\Delta V^{*\ddagger}_{intr}$ is an intrinsic volume change, i.e., the change in partial molar volume caused by lengthening of a metal-solvent bond and by partial formation of an entering ligand-metal bond, which is accompanied by a solvational volume change, $\Delta V^{*\ddagger}_{solv}$. However, since Hipt has no formal charge, its dipole, if any, may be small, ΔV_{os}° and $\Delta V^{*\ddagger}_{solv}$ may not be large,[7] and they may not differ much for the trivalent metal ions studied in this paper. Therefore, we think that the obtained values of activation volume reflect the intrinsic volume change for the complex formation.

It is noteworthy that the values of activation volume for complexation of Ga(III) and Fe(III) ions in water are quite different (4.0 and −8.7 cm^3 mol^{-1}, respectively), while those in Me_2SO are quite similar to each other ($\Delta V^\ddagger$/cm^3 mol^{-1}: 10.6 for Ga(III), 10.9 for Fe(III)). The entering ligand Hipt is neutral, the charge on both metal ions is +3, and their ionic radii are close to each other (r(Ga(III)) = 62 pm; r(Fe(III)) = 64 pm). Thus, this coincidence of the $\Delta V^\ddagger$ values would indicate that in Me_2SO their transition states should be geometrically very similar and that the intimate mechanism should be dissociative interchange (I_d) for both Ga(III) and Fe(III) ions.

In a less bulky solvent, i.e. water, both the complexation and solvent exchange at Fe(III) ion exhibit negative values of $\Delta V^\ddagger$, which are usually interpreted in terms of associative-interchange (I_a) mechanisms.[2] Thus the reaction may take place as if the metal-solvent bond was compelled to dissociate by the attack of an incoming ligand on the inner sphere of the metal ion. In bulkier solvents such as DMF and Me_2SO, we would expect a coordinated solvent to be forced to abandon partly the inner sphere of the metal ion, when an entering ligand starts to coordinate. Therefore, activation volumes for the Fe(III) ion largely vary depending on steric bulkiness of ligands and solvents.[2]

On the other hand, we have already demonstrated that in water the Ga(III) ion reacts through an I_d mechanism.[8] More recently the mechanism of the water exchange on $Al(H_2O)_6^{3+}$ has been demonstrated to be dissociative interchange.[9] For metal ions like Al(III) and Ga(III) ions, which react via a dissociative-interchange mechanism even in water, it is easy to dissociate the solvent molecule by a collision of reactants, so that the activation volumes vary to a lesser extent with bulkiness of ligands and solvents.

CPK models reveal that coordinated Me_2SO and DMF molecules shield the central metal ion more effectively than water and that Me_2SO molecules in the inner sphere would block the attack of an entering ligand more tightly than DMF. Such a situation has been confirmed, in the iron(III) system, by the fact that the activation volume for complexation of the iron(III) ion with Hipt increases with increasing bulkiness of coordinated solvent molecules: −8.7 cm^3 mol^{-1} for water,[10] 5.0 cm^3 mol^{-1} for DMF,[2] and 10.9 cm^3 mol^{-1} for Me_2SO[2] (see Table II). However, this is not the case for the In(III) system: the activation volumes for In(III) complexation are almost the same in both Me_2SO and DMF. This implies that the In(III) ion having a larger ionic radius than Fe(III) would be crowded to a similar extent with coordinated Me_2SO and DMF molecules.

The negative volume of activation for solvent exchange on the Fe(III) ion in Me_2SO and DMF indicates that the associative character is still maintained in these solvents. The activation volumes for complexation with Hipt in Me_2SO and DMF are more positive than the respective volume of activation for solvent exchange. It has been concluded that Hipt should be bulkier than Me_2SO and DMF as entering ligands. But this is not the case for Ga(III) complexation in Me_2SO. Since Ga(III) has an intimate dissociative character in water as described above, the activation volume varies to a lesser extent with different solvents.

As generally expected, the rate is higher for large metal ions (Table I). As is obvious from Table I, on going from Al(III) to Ga(III) to In(III) the activation volume for complexation in Me_2SO decreases. Larger metal ions tend to accept more easily an entering ligand: the larger the ionic radius, the less dissociative the mechanism. Quite similarly, the less bulky the solvent, the less dissociative the activation process. When we compare ions with isoelectronic configurations in the same column of the periodic table, the dissociative character of complex formation in a given solvent should decrease, as the activation enthalpy decreases, on going down the column.

Acknowledgment. Financial support from the Ministry of Education, Science, and Culture through a Grant-in-Aid for Scientific Research (No. 59430010) and a Grant-in-Aid for Special Project Research (No. 60129031) is gratefully acknowledged.

Registry No. $[Al(Me_2SO)_6](ClO_4)_3$, 16788-31-1; $[Ga(Me_2SO)_6](ClO_4)_3$, 29519-19-5; $[In(Me_2SO)_6](ClO_4)_3$, 58528-07-7; $[Al(DMF)_6](ClO_4)_3$, 16040-05-4; $[Ga(DMF)_6](ClO_4)_3$, 51921-91-6; $[In(DMF)_6](ClO_4)_3$, 13927-82-7; Al, 7429-90-5; Ga, 7440-55-3; In, 7440-74-6; 4-isopropyltropolone, 499-44-5.

Supplementary Material Available: Listings of numerical data of rate constants at various temperatures (Table SI) and at various pressures (Table SII) (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Ministero della Pubblica Istruzione
of Italy, Dipartimento di Chimica, University of Modena,
41100 Modena, Italy, Istituto di Chimica
Generale e Inorganica, Centro di Studi per la Strutturistica
Diffrattometrica del CNR, University of Parma,
43100 Parma, Italy, and Istituto di Chimica,
Facoltà di Medicina Veterinaria, University of Bari,
70126 Bari, Italy

Tridentate Facially Coordinated L-Aspartate Ion Complexation with the Copper(II) Ion: Spectroscopic and Structural Properties of Aqua(L-aspartato)(1,10-phenanthroline)copper(II) Tetrahydrate

L. Antolini,[1a] L. P. Battaglia,[1b] A. Bonamartini Corradi,[1b] G. Marcotrigiano,[1c] L. Menabue,*[1a] G. C. Pellacani,[1a] M. Saladini,[1a] and M. Sola[1a]

Received January 17, 1986

In solid complexes of copper(II) and aspartate of glutamate ions, thus far studied crystallographically, polymeric chain

Table I. Summary of Crystal Data Collection

(A) Crystal Parameters[a] at 20 °C

cryst syst: orthorhombic
a = 23.852 (2) Å
b = 11.731 (1) Å
c = 6.969 (1) Å
ρ(obsd) = 1.59 g cm^{-3}
ρ(calcd) = 1.583 g cm^{-3}

space group: $P2_12_12_1$ (D_2^4, No. 19)
V = 1949.98 Å^3
mol form: $C_{16}H_{23}CuN_3O_9$
mol wt: 464.93
Z = 4
$F(000)$ = 963.94

(B) Measurement of Data

radiation: Ni-filtered Cu Kα (λ = 1.541 78 Å)
reflecns measd: $+h,+k,+l$
scan type: ω–2ϑ
2ϑ limits: 4–140°
scan width: 1.1°
lowest scan speed: 2.5° min^{-1}
std: 1 every 50 reflecns (no changes)
no. of collcd reflecns: 2769
no. of obsd. reflecns: 2182 with $I \geq 3.0\sigma(I)$ ($\sigma^2(I)$ = (total counts) + (0.01 × intensity)^2)
cryst size: 0.29 × 0.26 × 0.20 mm
abs coeff: 19.2 (abs cor not applied)

[a] Unit cell parameters and their esd's were derived from a least-squares fit to the setting angles of 25 accurately centered reflections.

structures, where the amino acids bridge two or three different metal(II) ions, prevail in anhydrous or low-hydrate species, while isolated monomeric units, with the ligands acting as simple L-α-amino acids, are present in highly hydrated compounds.[2] In all cases the aspartate and glutamate ions always present an extended configuration, which favors square-planar or square-pyramidal copper(II) ion geometries.[2]

In solution, however, it is generally accepted that aspartate usually seems to act as a tridentate ligand toward the same metal ion.[3]

In this paper we report the synthesis and spectroscopic and structural investigations on the mononuclear aqua(L-aspartato)(1,10-phenanthroline)copper(II) tetrahydrate complex.

The results are discussed in comparison with the data obtained for the other mononuclear complexes aqua(L-aspartato)(2,2′-bipyridine)copper(II) trihydrate[4] and aqua(L-glutamato)(1,10-phenanthroline)copper(II) trihydrate,[2] previously investigated.

Experimental Section

Preparation of the Complex. The complex was prepared by dissolving Cu(L-asp)·$2H_2O$ (1 mmol), prepared as reported in ref 5, and *o*-phen (1,10-phenanthroline, 1.2 mmol) in water/ethanol (1:1, 20 mL). When the blue solution was allowed to stand for some days, blue crystals precipitated. Anal. Calcd for [Cu(L-asp)(*o*-phen)H_2O]·$4H_2O$, $C_{16}H_{23}CuN_3O_9$: C, 41.40; H, 4.78; N, 9.06; H_2O, 20.21. Found: C, 41.34; H, 4.62; N, 9.01; H_2O, 20.09.

Physical Measurements. Spectroscopic and magnetic measurements were made as reported in ref 2.

X-ray Crystallography. All data were collected on a Siemens AED four-circle diffractometer, at room temperature, by using Ni-filtered Cu Kα radiation.

Table I summarizes the details of crystal data collection and reduction.

Table II. Final Positional Parameters

atom	x/a	y/b	z/c
Cu	0.19558 (2)	0.17678 (4)	0.1995 (1)
N(1)	0.1939 (1)	0.3489 (3)	0.1921 (6)
C(1)	0.1509 (2)	0.4216 (4)	0.1970 (9)
C(2)	0.1578 (2)	0.5388 (4)	0.2025 (9)
C(3)	0.2105 (2)	0.5850 (3)	0.1997 (8)
C(4)	0.2569 (2)	0.5112 (3)	0.1957 (7)
C(5)	0.3142 (2)	0.5494 (4)	0.1969 (8)
C(6)	0.3568 (2)	0.4737 (4)	0.1808 (9)
C(7)	0.3467 (2)	0.3537 (4)	0.1656 (8)
C(8)	0.3886 (2)	0.2717 (4)	0.1344 (8)
C(9)	0.3740 (2)	0.1606 (4)	0.1143 (8)
C(10)	0.3179 (2)	0.1276 (3)	0.1246 (7)
N(2)	0.2770 (1)	0.2032 (3)	0.1528 (5)
C(11)	0.2920 (2)	0.3147 (3)	0.1703 (6)
C(12)	0.2464 (2)	0.3943 (3)	0.1894 (7)
O(1)	0.20237 (9)	0.0111 (2)	0.1853 (5)
O(2)	0.1521 (1)	−0.1400 (2)	0.1077 (6)
C(13)	0.1555 (2)	−0.0391 (3)	0.1527 (6)
C(14)	0.1024 (1)	0.0328 (3)	0.1726 (6)
N(3)	0.1157 (1)	0.1440 (3)	0.2595 (5)
C(15)	0.0742 (2)	0.0471 (4)	−0.0242 (6)
C(16)	0.1063 (2)	0.1137 (3)	−0.1757 (7)
O(3)	0.1532 (1)	0.1556 (3)	−0.1361 (5)
O(4)	0.0831 (1)	0.1224 (3)	−0.3377 (5)
Ow(5)	0.2204 (1)	0.1778 (3)	0.5401 (5)
Ow(6)	0.4793 (2)	0.6951 (4)	0.5953 (8)
Ow(7)	0.5275 (2)	0.1667 (4)	0.3586 (9)
Ow(8)	0.4471 (1)	0.2562 (3)	0.5946 (8)
Ow(9)	0.4859 (2)	0.4744 (4)	0.4551 (9)

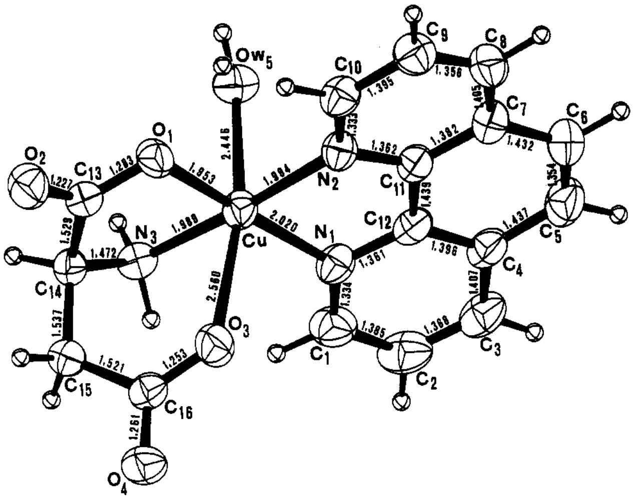

Figure 1. ORTEP view of the complex molecule showing the atom-numbering scheme, thermal motion ellipsoids (50%), and bond distances (Å). The range of esd's is as follows (Å): Cu–donor, ±0.003; C–O, ±0.004–0.005; C–N, ±0.005; C–C, ±0.005–0.007.

The structure was solved by standard Patterson and Fourier maps and refined by full-matrix least-squares calculation[6] with SHELX-76.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms belonging to organic ligands were fixed in calculated positions (C–H and N–H = 1.0 Å; $B_H = B_C$ or B_N + 1.0 Å^2) and allowed to ride on the atoms to which they were bonded. The water protons were treated as fixed contributors at locations obtained from difference maps (B_H = 6.5 Å^2). Least-squares refinement of this model led to final convergence at R = 0.040 and R_w = 0.045 ($w = 1.0/(\sigma^2(F) + 0.0049F_o^2)$]. The final difference map showed a maximum peak height of 0.55 e Å^{-3} near the Cu atom. During refinement, zero weight was assigned to five strong, low-order reflections, which may be affected by secondary extinction. The enantiomeric model was chosen by assigning the known *S* configuration, according to the Cahn–Ingold notation, to the optically active center of the L-aspartate ion.

Scattering factors for neutral atoms and corrections for anomalous dispersion were taken from ref 8. Major calculations were carried out on a VAX 11/750 computer. Final positional parameters for non-hydrogen atoms are reported in Table II.

Analyses. Nitrogen, carbon, and hydrogen were analyzed with a C. Erba Elemental Analyzer Instrument, Model 1106, by G. Goldoni, and

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(1) (a) University of Modena. (b) University of Parma. (c) University of Bari.

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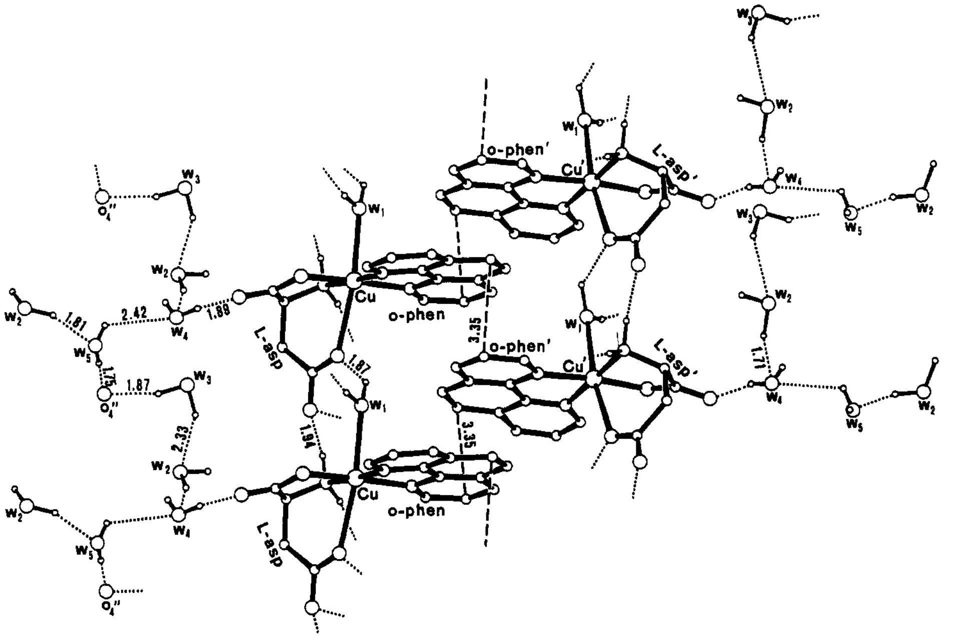

Figure 2. Crystal-packing diagram showing the shortest interatomic aromatic ring-stacking separations (dashed lines) and hydrogen-bonding interactions (dotted lines).

Table III. Selected Bond Angles (deg)

N(1)-Cu-N(2)	82.0 (1)	N(1)-Cu-O(1)	174.3 (1)
N(1)-Cu-N(3)	100.3 (1)	N(1)-Cu-O(3)	93.8 (1)
N(1)-Cu-Ow(5)	91.4 (1)	N(2)-Cu-O(1)	93.8 (1)
N(2)-Cu-N(3)	176.4 (1)	N(2)-Cu-O(3)	104.5 (1)
N(2)-Cu-Ow(5)	85.5 (1)	O(1)-Cu-N(3)	84.1 (1)
O(1)-Cu-O(3)	83.7 (1)	O(1)-Cu-Ow(5)	92.0 (1)
N(3)-Cu-O(3)	78.2 (1)	N(3)-Cu-Ow(5)	91.7 (1)
O(3)-Cu-Ow(5)	169.2 (1)	Cu-N(1)-C(1)	130.9 (3)
Cu-N(1)-C(12)	111.9 (2)	Cu-N(2)-C(10)	129.4 (3)
Cu-N(2)-C(11)	113.0 (2)	Cu-O(1)-C(13)	113.1 (2)
Cu-N(3)-C(14)	106.9 (2)	Cu-O(3)-C(16)	126.3 (3)

water was determined thermogravimetrically with a Mettler TA 3000 instrument.

Results and Discussion

The crystal structure consists of a discrete [Cu(L-asp)(*o*-phen)H_2O] unit and four lattice water molecules. The molecular geometry, the atom-numbering scheme, and bond distances of the complex molecule are shown in Figure 1. The molecular packing, mainly determined by hydrogen bonding and by aromatic ring-stacking interactions, is depicted in Figure 2. Selected bond angles are reported in Table III.

The copper atom shows elongated-rhombic-octahedral six-coordination. Its four closest ligand atoms are one O atom (α-carboxyl), the N atom (amino) from the α-glycinate moiety of the L-aspartate ion, and the two N atoms of the *o*-phen molecule. Their deviations from the best-fit plane, which range from +0.058 to −0.057 Å, indicate only a slight tetrahedral distortion, with the Cu atom, displaced 0.007 Å from the plane, lying at the center of this extremely flattened tetrahedron. The axial positions of the elongated octahedron are occupied by one water molecule at a bond distance of 2.446 (3) Å and by one β-carboxylate oxygen of the L-aspartate ion, thus acting as a tridentate ligand, at a bond distance of 2.560 (3) Å. These axial Cu–O bond lengths appear somewhat short in the rather wide range of previously reported values for octahedral Cu(II) complexes.[9,10] The largest distortions from ideal octahedral geometry involve the axial β-carboxylate O atom, whose bond direction deviates 13.6° from the normal to the equatorial coordination plane; the corresponding value for the apical water oxygen is 3.0°. It is of interest to note that this represents the first case of octahedral coordination by the Cu(II) ion in its L-aspartate and L-glutamate salts and amino adducts of known structure.[2,4,5,11]

Bond distances and angles within the *o*-phen molecule are normal.[12,13] The dihedral angles between the mean plane through the central six-membered C ring and those through the adjacent aromatic systems are 3.0 and 4.0°, respectively.

A new interesting structural result is the metal binding by the L-aspartate ion, which previous structural investigations have shown to act as a tridentate ligand only toward octahedral Zn(II),[14,15] Ni(II),[14,16,17] and Co(II)[14,18] cations. The L-aspartate and its parent L-glutamate ions were found to act as simply bidentate ligands (through their α-glycinate moiety), which give rise to mononuclear species, in their tetrahydrate complexes.[2,4] In addition, a second Cu atom is bridged by the β- or γ-carboxylate function in the anhydrous compounds, which show polymeric one-dimensional structures.[2] Further bridging by the second α-carboxylate oxygen produces two-dimensional polymeric structures in the dihydrate derivatives.[5,11] Present results confirm a previously suggested correlation between the coordination ability of these amino acidate anions and the water contents in their Cu(II) complexes.[2] As expected for a highly hydrated form, the present complex contains mononuclear discrete molecules, but either the metal binding by the amino acidate ion or the Cu coordination geometry differs from those observed in mononuclear complexes with the lower metal/ligand/water ratio 1/1/4.

The crystal packing is determined by a complex network of hydrogen-bond interactions involving carboxylate oxygens, amino groups, and water molecules and by aromatic ring-stacking interactions[13,19,20] between *o*-phen ligands (Figure 2). Their mean

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planes make a dihedral angle of 11.0°, and these interactions appear weaker than those observed in the [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ complex,[2] where the dihedral angle between aromatic ring planes is 1.4°.

The complex is stable in air and presents a thermogravimetric behavior corresponding to the loss of uncoordinated and coordinated water molecules in the 35–120 °C temperature range. In the square-pyramidal [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ complex[2] the coordinated water molecule is lost in the 110–150 °C temperature range, indicating a greater bond strength of the coordinated water molecule in a square-pyramidal than in a tetragonally distorted octahedral environment.

The room-temperature magnetic moment of the complex (μ_{eff}(293 K = 1.84 μ_B) is "normal" and typical of "magnetically dilute" complexes;[21] its polycrystalline EPR spectrum ($g_\parallel = 2.33$; $g_\perp = 2.08$) closely resembles those of copper(II) complexes having similar environments and chromophores, reported in the literature,[21,22] for which an essentially $d_{x^2-y^2}$ ground state has been suggested.

The room-temperature electronic spectrum of the complex presents a broad d–d band with an unsymmetrical maximum centered at 16400 cm^{-1}, typical of CuN_3O_3 chromophores.[23,24]

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Registry No. [Cu(L-asp)(*o*-phen)H_2O]·$4H_2O$, 102649-32-1.

Supplementary Material Available: Listings of atomic temperature factors, hydrogen atom parameters, complete bond distances and angles, hydrogen-bonding distances and angles, ring-stacking interactions, and selected least-squares planes (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratory
of Analytical Chemistry, Faculty of Science,
Nagoya University, Chikusa, Nagoya 464, Japan

Kinetic Study of Acetic Acid Exchange on Manganese(II), Cobalt(II), and Copper(II) Acetates in Acetic Acid by Oxygen-17 Nuclear Magnetic Resonance[1]

Akiharu Hioki,[†] Shigenobu Funahashi,* and Motoharu Tanaka

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We have previously studied acetic acid exchange on perchlorates of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) ions in acetic acid (HOAc).[2] These metal(II) perchlorates in acetic acid exist as hexasolventometal ions that form ion pairs with perchlorate anion. On the other hand, acetate ion (OAc^-) in transition-metal(II) acetates is bound to the central metal ions in acetic acid.[3,4] Thus, we expect that coordinated acetate ion exerts some effect on the solvent-exchange rate, i.e., bound-ligand effect. In this work rates of acetic acid exchange on $Mn(OAc)_2$, $Co(OAc)_2$, and $Cu_2(OAc)_4$ (tetrakis(μ-acetato)dicopper(II)) in acetic acid and mixtures with dichloromethane-d_2 as an inert cosolvent were measured by means of the oxygen-17 NMR line-broadening method. The activation parameters obtained are compared with those for the corresponding perchlorates.[2]

Experimental Section

The purification of acetic acid and dichloromethane-d_2 (CD_2Cl_2) and the preparation of oxygen-17-enriched acetic acid were described previously.[2,5-8] The percentage of oxygen-17 in the oxygen-17-enriched acetic acid is 5.13 atom % of all oxygen atoms. The mean molecular weight of this oxygen-17-enriched acetic acid is 60.53. Tetrasolventomanganese(II) acetate was prepared by adding the stoichiometric amount of acetic anhydride to the tetrahydrate dissolved in acetic acid and allowing the reaction to occur at room temperature for 2 weeks.[4] The obtained crystal was washed with acetic anhydride and acetic acid. The resultant pale pink compound may be formulated as $Mn(OAc)_2(HOAc)_4$. The compound, dried in a desiccator over sodium hydroxide for 1 week under reduced pressure, should be $Mn(OAc)_2(HOAc)$, which was confirmed by the analysis for manganese (calcd, 23.57%; found, 23.55%). Hydrated cobalt(II) acetate (reagent grade) was recrystallized from distilled water. The hydrate was dissolved in acetic acid. In order to eliminate the water, excess acetic anhydride was added to the cobalt(II) acetate solution. After this solution was allowed to stand at 80 °C for 3 days, anhydrous cobalt(II) acetate precipitated. This red crystal was recrystallized from acetic acid and may be formulated as $Co(OAc)_2(HOAc)_4$. The crystals were dried at 120 °C for 3 h to obtain $Co(OAc)_2$. The quantitative change of $Co(OAc)_2(HOAc)_4$ to $Co(OAc)_2$ was confirmed thermogravimetrically (Shimadzu thermal analyzer DT-30). Tetrakis(μ-acetato)dicopper(II) disolvate ($Cu_2(OAc)_4(HOAc)_2$, dimeric copper(II) acetate) was prepared as described previously.[5] It was dried in a desiccator over sodium hydroxide for a few days under a reduced pressure. The determination of copper in the dried copper(II) acetate crystals by both electrolysis and EDTA titration confirmed the composition of $Cu_2(OAc)_4$.

^{17}O NMR spectra were obtained with use of JNM-FX60, JNM-FX90QE, and JNM-GX400 (JEOL Ltd.) instruments operating at 8.16, 12.15, and 54.21 MHz, respectively. ^1H NMR spectra were observed at 60 MHz on a JNM-C-60H NMR spectrometer (JEOL Ltd.). The preparation of NMR samples and the NMR measurement have been described in our previous paper.[8] The compositions of samples for the NMR measurement are tabulated in Table I.

The temperature dependence of the observed transverse relaxation rate, $1/T_{2P}$, corrected for the ligand relaxation rate in the absence of the metal complex, can be analyzed by the modified Swift and Connick equation (eq 1),[9-11] where symbols have the usual meaning.[8] The analysis of data was carried out by the least-squares program SALS.[12]

$$(T_{2P}P_M)^{-1} = \frac{1}{\tau_M}\,\frac{T_{2M}^{-2} + (\tau_M T_{2M})^{-1} + (\Delta\omega_M)^2}{(\tau_M^{-1} + T_{2M}^{-1})^2 + (\Delta\omega_M)^2} + \frac{1}{T_{2O}} \qquad (1)$$

Results

All NMR data for line broadening are tabulated in Tables s-I and s-II (supplementary material).

Manganese(II) Acetate. The temperature dependence of line widths log $(T_{2P}P_M)^{-1}$ for manganese(II) acetate is represented in Figure 1. It is reasonable that the chemical-exchange region, where τ_M^{-1} contributes to the line width to a large extent, is identical at 8.16, 12.15, and 54.21 MHz for the sample of 20.4 wt % HOAc. NMR and kinetic parameters for a nonlinear least-squares fitting are given in Table s-III (supplementary

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[†] Present address: The National Chemical Laboratory for Industry, Yatabe, Ibaraki 305, Japan.

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