Saccharinate as a Versatile Polyfunctional Ligand. Four Distinct Coordination Modes, Misdirected Valence, and a Dominant Aggregate Structure from a Single Reaction System

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The reaction system consisting of copper, saccharinate, and the auxiliary ligands H_2O, PPh_3, and NH_3 produces a sequence of compounds in which saccharinate is coordinated to copper in four distinct manners. The complex *trans*-[Cu(sacch)$_2$(H$_2$O)$_4$] (**2**) (produced by thermal dehydration of *trans*-[Cu(sacch)$_2$(H$_2$O)$_4$]·2H$_2$O (**1**)) reacts with triphenylphosphine in CH$_2$Cl$_2$ to produce any or all of three Cu(I) complexes, depending upon conditions. The three Cu(I) compounds are Cu(sacch)(PPh$_3$)$_3$ (**3**), in which saccharinate binds to copper through the carbonyl group of the ligand, Cu(sacch)(PPh$_3$)$_2$ (**4**), in which sacch binds to Cu through its charge-bearing nitrogen atom; and [Cu(sacch)(PPh$_3$)]$_2$ (**5**), a dinuclear complex in which saccharinate bridges two Cu centers through its imidate nitrogen and carbonyl oxygen atoms. Complexes **3**−**5** can be isolated individually, although in solution they exist in a complex equilibrium which has been examined by NMR spectroscopy. Each of the three Cu(I) products reacts with NH$_3$ in CH$_2$Cl$_2$ solution to produce *trans*-[Cu(sacch)$_2$(NH$_3$)$_4$] (**6**), an unstable Cu(II) complex that exhibits misdirected valence at the Cu−N(sacch) bond. Complex **6** evolves spontaneously to [Cu(sacch)(NH$_3$)$_4$]-(sacch)·H$_2$O (**7**), which in the solid state is dominated by a supramolecular aggregate of two formula units, linked by hydrogen bonding in which the water molecule plays a central role. Alternative pathways exist to several of the products. The X-ray crystal structure analyses of **3**−**7** are reported and establish the coordination modes of saccharinate, the misdirected valence in **6**, and the supramolecular aggregation in **7**. The structure analysis of **7** by single-crystal neutron diffraction is reported and together with the previously reported neutron structure analysis of **1** establishes the substitution of the auxiliary ligand H$_2$O by NH$_3$ in the Cu(II) products.

Introduction

Saccharine and saccharinate have been studied in detail in several scientific contexts, largely because of their commercial use in noncaloric food sweeteners. While the large majority of studies on saccharine have been related to the gustatory responses that it evokes, and to possible carcinogenesis and DNA-altering ability,[1] research has been conducted into quite varied properties and uses of saccharine, such as in molecular materials[2a−c] and metallurgy.[2d]

Our own interest in saccharine and saccharinate lies in the use of the latter as a polyfunctional ligand in transition-metal chemistry. Polyfunctional ligands—ligands of a predominantly organic nature that possess several functional groups—are capable of being ligated to metal centers and, at the same time, of forming relatively strong interactions with a crystalline environment, mostly through hydrogen bonding. The often countermanding energetic requirements of the crystalline surroundings and the transition-metal center can generate stresses that lead to the stabilization of species, stoichiometries, or conformations which in solution would not be expected to predominate.

Complexes of polyfunctional ligands thus serve as probes into several interesting phenomena, as well as being potential sources of new molecular materials. We have observed, for example, changes in the expression of the Jahn−Teller effect in molecular solid solutions of a chromium nicotinate complex dissolved in the solid in a zinc−nicotinate host (nicotinate = *m*-carboxylatopyridine).[3a,b] With saccharinate, we have observed that *trans*-[Cr/Zn(sacch)$_2$(H$_2$O)$_4$]·2H$_2$O (sacch = saccharinate, C$_7$H$_4$NO$_3$S$^-$, **I**), forms molecular solid solutions in which the anisotropic

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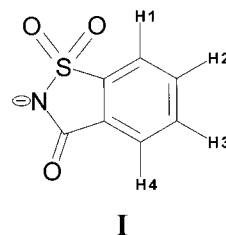
displacement parameters derived from diffraction data indicate a subtle, progressive disorder, as a function of chromium concentration, in the ligand atoms affected by Jahn−Teller

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distortion.[3c,d] The intramolecular strain created in each case is the result of intermolecular interactions involving the polyfunctional ligands and mediated largely by hydrogen bonding. The same intramolecular strain has also been introduced into systems not containing polyfunctional ligands, such as solid solutions of the chromium and zinc ammonium Tutton salts[4] $(NH_4)_2[Cr_x-Zn_{1-x}(H_2O)_6](SO_4)_2$ and single crystals of chromium or copper hexahydrate hexafluorosilicate.[5]

The coordination chemistry of saccharinate as a ligand, meanwhile, has been explored for several transition metals. Saccharinate (*o*-sulfobenzoimidate), which has sulfonyl and carbonyl groups as well as a charge-bearing nitrogen atom in its five-membered ring, is already known to be able to ligate to metal atoms through any of these moieties, as well as to bridge two transition metals through the amidato-like $-NC=O$ system. The most common coordination mode is ligation through the nitrogen atom, which has been observed in hydrates of the 3d series, as well as in mercury saccharinate.[6] Saccharinate has also been found to bind through the carbonyl oxygen in a hydrate of neodymium[7] and in a pyridine adduct of vanadium,[6b] in which it appears that steric hindrance impedes binding through the ring nitrogen atom. As a three-atom amidato-like moiety, saccharinate is able to bridge a long Cr−Cr quadruple bond,[8] and it has also been observed to bridge a dinuclear copper complex.[9] The most unusual contact so far observed between saccharinate and a metal atom is what might be described as semicoordination to lead—a weak contact which may possess some degree of covalency—through a sulfonyl oxygen atom, an atom not expected to be sufficiently basic to coordinate.[10] Theoretical and spectroscopic studies have been reported in which nuances in the spectroscopic properties and structural features of saccharinate have been related to its coordination modes.[11]

In this report we describe a reaction system that produces complexes of saccharinate displaying all four coordination modes, including semicoordination through a sulfonyl oxygen

atom in a solid-state system dominated by a supramolecular aggregate. In this series of products, the coordination properties of saccharinate are adapted on a case-by-case basis to the steric properties of the complex and/or to the stabilization of the crystalline environment.

Experimental Section

Solvents and Reagents. Solvents were dried over a Na amalgam and distilled under nitrogen before use unless otherwise stated. Elemental analyses were carried out on a Perkin-Elmer 240B microanalyzer. IR spectra (4000 to 200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^{1}H (300.13 MHz), ^{13}C{^{1}H} (75.47 MHz), and ^{31}P{^{1}H} (121.49 MHz) NMR spectra were recorded in CDCl$_3$, CD$_2$Cl$_2$, or C$_6$D$_5$CD$_3$ solutions, at the temperatures stated in the text, on a Bruker ARX300 spectrometer. ^{1}H and ^{13}C{^{1}H} spectra were referenced using the solvent signals as internal standard, and ^{31}P{^{1}H} spectra were externally referenced to H$_3$PO$_4$ (85%). Mass spectra (positive ion FAB) were recorded on a VG AutoSpec spectrometer. In-solution molecular weight measurements were performed on a Knauer vapor pressure osmometer over CDCl$_3$ solutions.

Syntheses. Compound **1**, [Cu(sacch)$_2$(OH$_2$)$_4$]·2H$_2$O, was prepared as previously published elsewhere.[6a] Complex **2** has been described[12] as the dehydrated product [Cu(sacch)$_2$(H$_2$O)$_4$], although it has not been fully characterized.

[Cu(sacch)(PPh$_3$)$_3$] (3). Over a refluxing solution of 0.2 g (0.8 mmol) of PPh$_3$ in 40 mL of CH$_2$Cl$_2$ was added 0.1 g (0.2 mmol) of **1** that had previously been desiccated in an oven at 120 °C for 24 h (this heating converts **1** into **2**). The greenish blue suspension was refluxed with stirring for 12 h, until it had become a colorless solution. The solution was washed with several aliquots of diethyl ether in order to eliminate the excess of PPh$_3$ and was then dried under vacuum. The white powder isolated was air stable. Yield: 0.15 g (73%). Anal. Calcd: H, 4.73; C, 70.98; N, 1.34; S: 3.07. Found: H, 4.51; C, 70.39; N, 1.33; S, 3.21. IR (cm^{-1}): 1612 s, 1586 s, 1153 s, 750 s, 743 m, 603 s, 544 s. See the structure of compound I in the Introduction for a labeling scheme for NMR assignments. ^{1}H NMR (ppm): 7.75 (d, 1H, H(4)), 7.60 (d, 1H, H(1)), 7.58−7.50 (m, 2H, H(2), H(3)), 7.34−7.19 (m, 45H, H-phosphines). ^{31}P{^{1}H} NMR (ppm): 166.36 (all phosphorus atoms are chemically equivalent in solution). ^{13}C{^{1}H} NMR (ppm): 166.36 (C(1)), 142.18 (C(7)), 131.35 (C(2)), 130.59 (C(4)), 130.31 (C(5)), 121.84 (C(3)), 118.50 (C(6)), 132.47−132.25 (C-*ortho* PPh$_3$), 132.04−132.77 (C-*ipso* PPH$_3$), 128.11 (C-*para* PPh$_3$), 127.07 (C-*meta* PPh$_3$). Crystals were obtained by slow evaporation of a solution of **3** in CH$_2$Cl$_2$.

[Cu(sacch)(PPh$_3$)$_2$] (4) Method a. To a solution of 0.40 g (0.61 mmol) of [Cu(PPh$_3$)$_2$(NO$_3$)] in 30 mL of CH$_2$Cl$_2$ was added 0.13 g (0.61 mmol) of Nasacch·H$_2$O (molar ratio 1:1). The suspension was kept stirring for 12 h, after which the NaNO$_3$·nH$_2$O formed was removed by filtration. The solution was then reduced to dryness under vacuum, and the solid obtained was washed several times with *n*-pentane and dried. The white powder is air-stable. Yield: 0.44 g (94%).

Method b. Treatment of **1** with 3 equiv of PPh$_3$ under the same reaction conditions as those used for **3** or **5** generated mixtures of **3, 4,** and **5,** from which **4** was isolated in low yields. Anal. Calcd: H, 4.38; C, 67.07; N, 1.79; S, 4.1. Found: H, 4.07; C, 65.62; N, 1.73; S, 3.49. IR (cm^{-1}) 1661 s, 1589 m, 1285 s, 1250 m, 1158 s, 1152 m, 1120 m, 1095 s, 965 m, 782 w, 745 s, 706 s, 601 s, 529 m, 518 s, 505 s, 394 w. ^{1}H NMR (ppm): 7.75 (d, 1H, H(4)), 7.61 (d, 1H, H(1)), 7.58−7.51 (m, 2H, H(2), H(3)), 7.34−7.16 (m, 30H, H-phosphine). ^{13}C{^{1}H} NMR (ppm): 167.79 (C(1)), 143,53 (CV(7)), 132.73 (C(2)), 132.07 (C(4)), 131.79 (C(5)), 131.18 (C(3)), 119.94 (C(6)), 133.80 (C-*ortho* PPh$_3$), 131 (over C(5)) (C-*ipso* PPh$_3$), 129.98 (C-*para* PPh$_3$), 128.65 (C-*meta* PPh$_3$). ^{31}P{^{1}H} NMR (ppm): −0.713 (all phosphorus atoms are equivalent in solution). Good-quality crystals can be obtained by careful

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Table 1. Crystal Data for Cu(sacch)(PPh$_3$)$_3$ (**3**), Cu(sacch)(PPh$_3$)$_2$·$^3/_4$CHCl$_3$ (**4**·$^3/_4$CHCl$_3$), [Cu(sacch)(PPh$_3$)]$_2$·CH$_2$Cl$_2$ (**5**·CH$_2$Cl$_2$), *trans*-[Cu(sacch)$_2$(NH$_3$)$_4$] (**6**), and [Cu(sacch)(NH$_3$)$_4$](sacch)·H$_2$O (**7**)

	3	4	5	6	7	
					X-ray	neutron
formula	CuC$_{61}$H$_{49}$P$_3$NO$_3$S	C$_{43}$H$_{34}$CuNO$_3$P$_2$S·$^3/_4$CHCl$_3$	C$_{50}$H$_{38}$Cu$_2$N$_2$O$_6$P$_2$S$_2$·CH$_2$Cl$_2$	C$_{14}$H$_{20}$CuN$_6$O$_6$S$_2$	C$_{14}$H$_{22}$CuN$_6$O$_7$S$_2$	
fw	1032.52	859.02	1100.89	496.02	514.04	
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	triclinic	
space group	*Pbca*	*P*1̄	*C*2/*c*	*P*2$_1$/*c*	*P*1̄	
cryst color	colorless	colorless	colorless	sky blue	royal blue	
a (Å)	20.294(3)	13.3164(2)	19.8920(13)	7.374(2)	7.045(1)	6.998(1)
b (Å)	19.784(2)	14.1508(2)	16.6168(10)	12.775(3)	10.578(2)	10.528(2)
c (Å)	24.974(3)	23.6548(4)	15.2411(8)	10.327(3)	13.967(3)	13.881(2)
α (deg)	90	80.8106(9)	90	90	98.05(3)	97.55(2)
β (deg)	90	86.3813(8)	90.561(8)	98.94(3)	92.39(3)	92.46(2)
γ (deg)	90	78.8322(8)	90	90	99.08(3)	99.35(2)
V (Å^3)	10027(2)	4314.54(12)	5037.6(5)	961.1(5)	1015.5(3)	998.1(2)
temp (K)	293(2)	295(2)	293(2)	298(2)	293(2)	20(1)
Z	8	4	4	2	2	2
R1^a	0.1040	0.0709	0.0370	0.1042	0.0296	0.098^d
wR2^b	0.1984	0.2152	0.0992	0.1967	0.0692	0.057^e
GOF^c	0.961	1.019	1.031	1.022	1.045	1.896

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, calculated using reflections with $(F_o)^2 > 2\sigma[(F_o)^2]$. ^{b} wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, for all reflections used in the refinement. ^{c} GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, for all reflections used in the refinement; n = no. of observations; p = no. of parameters. ^{d} R(F) = $\sum||F_o| - |F_c||/\sum|F_o|$, using reflections with $F_o > 3\sigma(F_o)$. ^{e} R$_w$(F) = $[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, for all reflections used in the refinement to the neutron data ($F_o > 3\sigma(F_o)$).

evaporation of a concentrated solution of [Cu(sacch)(PPh$_3$)$_2$] in CHCl$_3$ under a reduced-pressure N$_2$ atmosphere.

[Cu(sacch)(PPh$_3$)]$_2$ (5). The method used was the same as that for **3**, using 0.16 g (0.33 mmol) of **1** (previously desiccated in an oven at 120 °C) and 0.17 g (0.66 mmol) of PPh$_3$. Compound **5** is stable as a white powder if kept dry; the colorless solution of **5** is oxidized within several hours if left open to the air. Anal. Calcd: H, 3.68; C, 59.12; N, 2.69; S, 6.17. Found: H, 3.89; C, 59.05; N, 2.74; S, 6.17. IR (cm^{-1}): 1637 vs, 1591 m, 1307 s, 1262 m, 1168 m, 1157 s, 1124 s, 734 m, 694 m, 678 m, 596 m, 530 m, 394 m. ^{1}H NMR (ppm): 7.57 (d, 1H, H(4)), 7.60(d, 1,1 H(1)), 7.58−7.51 (m, 2H, H(2), H(3)), 7.32−7.16 (m, 16H, H-phosphines). ^{31}P{^{1}H} NMR (ppm): −1.26 (all phosphorus atoms are equivalent in solution). ^{13}C{^{1}H} NMR: 167.68 (C(1)), 143.55 (C(7)), 132.71 (C(2)), 132.05 (C(4)), 131.80 (C(5)), 123.28 (C(3)), 119.94 (C(6)), 133.77 (C-*ortho* PPh$_3$), 132.71−132.05 (C-*ipso* PPh$_3$), 129.85 (C-*para* PPh$_3$), 128.61 (C-*meta* PPh$_3$). Crystals for X-ray analysis were obtained by slow diffusion of *n*-pentane into a dilute solution of **5** in CH$_2$Cl$_2$.

[Cu(sacch)$_2$(NH$_3$)$_4$] (6). This rather unstable complex was isolated by crystallization in an inert atmosphere using Schlenk techniques. A colorless solution of **3** in freshly distilled CH$_2$Cl$_2$ was kept at +3 °C under a constant pressure of NH$_3$ (g). After 16 h under these conditions a crop of small, flat crystals of **6** can be harvested from a solid residue, the other components of which have not been identified. These crystals must be collected in the absence of air; otherwise, they evolve to **7**. This evolution of **6** to **7** takes place both in CH$_2$Cl$_2$ solution in the presence of air and in the solid state in the presence of air, once the crystals have been isolated from solution. The formation of compound **7** can easily be monitored by the difference in color of the crystals (**6** is sky blue, **7** is royal blue). IR for **6** (cm^{-1}): 3355 vs, 1686−1612 vs, 1332 m, 1288 s, 1258 vs, 1236 vs, 1142 vs, 1137 vs, 1117 vs, 1053 s, 965 vs, 797 w, 774 m, 757 s, 634 s, 603 s, 546 s, 532 s, 402 m, 346 m. Because of the insolubility of **6** in most common solvents, no physical or spectroscopic measurements were made in solution.

[Cu(sacch)(NH$_3$)$_4$](sacch)·H$_2$O (7). Method a. NH$_3$(g) was bubbled through a solution of 0.15 g (0.60 mmol) of CuCl$_2$·6H$_2$O in 30 mL of EtOH until the solution became dark blue. Once the species [Cu-(NH$_3$)$_4$]$^{2+}$ had been thus formed, 0.26 g (1.2 mmol) of Na(sacch)·H$_2$O was dissolved in 30 mL of MeOH/EtOH (20/80) and added to the dark blue solution with constant stirring. After 10 min the product precipitated as a dark blue microcrystalline powder. Yield: 75%.

Method b. In a solution of 0.26 g (0.48 mmol) of [Cu(sacch)$_2$-(H$_2$O)$_4$]·2H$_2$O (**1**) in 30 mL of EtOH or THF was bubbled NH$_3$(g).

The light blue suspension gave way to a dark blue precipitate that was filtered and isolated. Yield: 0.23 g (95%).

Method c. A colorless solution of [Cu(sacch)(PPh$_3$)$_x$] ($x = 1−3$; **5**, **4**, **3**) in 30 mL of CH$_2$Cl$_2$ was kept under a constant pressure of 1.0 bar of NH$_3$(g). The initial product, **6**, quickly evolves to **7**, which can be isolated in high yield. Anal. Calcd: H, 4.31; C, 32.71; N, 16.35, S, 12.47. Found. H, 4.09; C, 32.27; N, 16.10; S, 12.43. IR (cm^{-1}): 3610 m, 3351 vs, 3181 s, 1668−1587 vs, 1271 vs, 1227 s, 1154 vs, 1119 vs, 1054 s, 970 vs, 957 s, 786 s, 772 m, 747 s, 676 s, 648 m, 633 m, 604 s, 544 s, 532 s, 461 w, 401 m, 339 m. A large crop of high-quality crystals can be obtained from the mother liquor of any of the preparations (method a, b, or c) after 48 h or by recrystallization of **7** in concentrated aqueous ammonia. Larger crystals for use in the neutron diffraction experiment were obtained from solutions produced by methods a and b, after 2 weeks at room temperature.

X-ray Structure Analyses. All data for the five structures were collected at room temperature (Table 1). A Stoe AED2 four-circle diffractometer[13] was used for the data collection for complex **7**, a Nonius CAD-4 was used for **3**, **5**, and **6**,[14] and a Nonius KappaCCD was used for **4**.[14]

After data reduction and application of absorption corrections, the structures were solved by either Patterson interpretation or direct methods[15] and were refined by full-matrix least-squares.[16] For the structure of **4**, for which two independent molecules were found in the asymmetric unit of the triclinic cell, a further test for higher symmetry was conducted; a list of F_o and F_c, ordered on 2θ, was examined visually

(13) Stoe AED-4 control program: DIF4; Stoe & Cie GmbH, Darmstadt, Germany.

(14) (a) CAD-4 control program: CAD4/PC Version 1.5c (1994) and Version 2.0 (1996), Nonius BV, Delft, The Netherlands. (b) KappaCCD control program: Collect, 1997−2000, Nonius BV, Delft, The Netherlands.

(15) (a) Data were processed on a Local Area VAXCluster (VMS V5.5-2) using the commercial package SHELXTL-PLUS Release 4.21/V (1990), Siemens Analytical X-ray Instruments, Inc., Madison, WI, and on an AlphaStation 200 4/166 (OpenVMS/Alpha V6.2) using the commercial package SHELXTL Relat. 5.05/VMS (1996), Siemens Analytical X-ray Instruments, Inc., Madison, WI. Further calculations were done on a Hewlett-Packard 9000 Model 715/50 (HP-UX V9.05 and V10.20). (b) AED-4 data reduction: REDU4 Rev. 7.03; Stoe & Cie GmbH, Darmstadt, Germany. (c) Data reduction for the CAD-4: XCAD4B (K. Harms, 1996). (d) Data reduction for the KappaCCD: HKL Denzo and Scalepack (Otwinowski & Minor, 1997). (e) Structure solution: Sheldrick, G. M. SHELXS-86: Fortran Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.

for systematic pairing of similar intensities. Such pairing, which would be present if the Laue group were really of higher symmetry, was not observed. The distinct conformational parameters involving the phenyl groups at the peripheries of the two molecules served to verify their crystallographic independence.
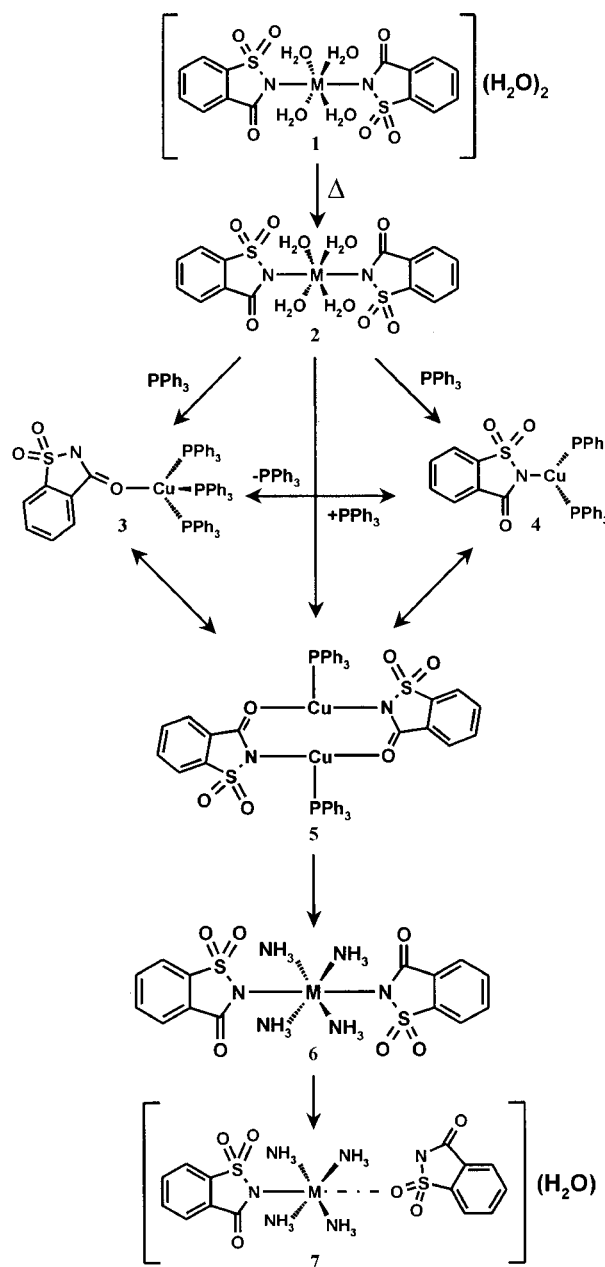
Neutron Experiment. Neutron diffraction data were collected on the Single Crystal Diffractometer (SCD) beam line at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The SCD, a time-of-flight energy-dispersive diffractometer, is equipped with a spatially fixed, time- and position-sensitive detector containing a ^{6}Li glass scintillator with dimensions of 30×30 cm^2. The SCD instrument uses the entire thermal spectrum of neutrons from each pulse of the 30 Hz IPNS spallation source. For a given crystal setting, data are stored in three-dimensional histograms which comprise measurements of blocks of reciprocal space. Each point in a given histogram has coordinates x, y, and t, which are the horizontal and vertical detector positions and the time of flight, respectively. Time of flight, t, is related to the neutron wavelength λ by the de Broglie equation $\lambda = (h/m)(t/l)$, in which h is Planck's constant, m is the neutron mass, and l is the path length traversed in time t. The 120 time-of-flight channels in each histogram, which correspond to neutron wavelengths in the range of 0.7−4.2 Å, are constructed in such a way that $\Delta t/t$ has a constant value of 0.015. The details of the SCD instrument and beamline, along with data collection and analysis procedures, have been described previously.[17,18] The temperature of the sample is controlled by a Displex closed-circuit He refrigerator (Air Products and Chemicals, Inc. Model CS-202).

For [Cu(sacch)(NH$_3$)$_4$](sacch)·H$_2$O (**7**) the orientation matrix of the crystal was obtained from an automated autoindexing algorithm[19] using the peaks in one histogram. In all, 40 histograms were measured, covering half of reciprocal space. The Bragg peaks in each histogram were integrated in three dimensions about their predicted positions and corrected for the incident beam spectral dispersion and detector efficiency. Lorentz and absorption corrections were also applied. The initial structural model consisted of the atomic coordinates for all of the non-hydrogen atoms, taken from the X-ray structure determination. This model was refined using isotropic displacement parameters, and then all hydrogen atoms were located in a difference Fourier map. For the final refinement, an extinction correction was included; with the exception of one sulfonyl sulfur atom, all atoms including hydrogen were refined anisotropically using the program GSAS.[20]

Results

In the three Cu(I) complexes **3**−**5**, saccharinate adopts three distinct coordination modes, occupying a lesser fraction of the space immediately around the metal as the number of triphenylphosphine ligands increases. In the unstable Cu(II) complex **6**, the saccharinate ligand is only weakly coordinated through N, and in the very stable Cu(II) complex **7**, which evolves from **6**, one saccharinate is N-coordinated and another participates in a dominant aggregate structure while making a weak contact to the copper center through one of the sulfonyl oxygen atoms. Scheme 1 shows the saccharinate coordination modes that are displayed in the Cu/sacch/{H$_2$O,PPh$_3$,NH$_3$} reaction system. It is possible, beginning with complex **1**, [Cu(sacch)$_2$(H$_2$O)$_4$]· 2H$_2$O, to traverse the entire system synthetically, with alternative pathways through the Cu(I) complexes, before arriving at compound **7**. As described below, the three Cu(I) complexes

(16) (a) Sheldrick, G. M.; SHELXL-93: FORTRAN-77 Program for the Refinement of Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Germany, 1993. (b) Sheldrick, G. M. SHELXL-97: FORTRAN Program for Crystal Structure Refinement, 1997.
(17) Schultz, A. J.; Van Derveer, D. G.; Parker, D. W.; Baldwin, J. E. *Acta Crystallogr., Sect. C* **1990**, *C46*, 276−279.
(18) Schultz, A. J. *Trans. Am. Crystallogr. Assoc.* **1987**, *23*, 61−69.
(19) Jacobson, R. A. *J. Appl. Crystallogr.* **1986**, *19*, 283−286.
(20) Larson, A. C.; Von Dreele, R. B. GSAS-General Structure Analysis System; Los Alamos National Laboratory, Los Alamos, NM, 1994.

Scheme 1

appear to establish an equilibrium in solution, and the predominance of one or the other depends on the specific conditions imposed.

The topologies of the different coordination modes will be described with reference to the crystal structure determinations. In compound **3**, [Cu(sacch)(PPh$_3$)$_3$], in which the presence of three ligated PPh$_3$ groups imposes the greatest steric hindrance to saccharinate coordination found in any of these complexes, the saccharinate adopts the full coordination mode that puts its bulk farthest from the metal, namely coordination through the carbonyl oxygen atom (Figure 1). Unlike the sulfonyl semicoordination mode found for **7** (see below), binding through C= O in this case involves an intimate contact at a short distance (Cu(1)−O(1) = 2.113 (8) Å). The remaining coordination sites in the distorted tetrahedron about copper are occupied by the three phosphorus atoms of the three PPh$_3$ ligands. Distances and angles around the metal center are listed in Table 2. It is possible, alternatively, to view the coordination about the copper center as a triangular pyramid with the ligated oxygen atom at

Figure 1. Drawing of Cu(sacch)(PPh₃)₃ (**3**), indicating the atom-labeling scheme. Phenyl hydrogen atoms have been omitted. Saccharinate hydrogen and phenyl carbon atoms are drawn as circles. Other atoms are represented by their 50% probability ellipsoids.

the apex. The triangular base formed by the three P atoms is nearly equilateral; the copper atom is approximately 0.5 Å above the base, and the Cu−O vector makes an angle of 13.6° with the line perpendicular to the base. The three Cu−P distances (average value 2.347[13] Å)[21] are significantly longer than Cu−O.

Compound **4**, Cu(sacch)(PPh₃)₂, is a three-coordinate Cu(I) complex in which the presence of only two bulky PPh₃ ligands permits the saccharinate to move in closer, binding now through its imido nitrogen atom at a distance of approximately 2.0 Å (Table 2). This arrangement binds saccharinate to copper directly through an atom of the ring system of the ligand, rather than through an atom one bond displaced from it, as is the case in complex **3**. The crystallographic asymmetric unit of **4** consists of two independent, but chemically nearly identical, molecules of the neutral complex. The major differences between the two molecules lie in the relative orientations of the phenyl rings, which are not of central importance for present purposes. A drawing of one molecule is shown in Figure 2. The planar coordination environment about the copper center deviates in two ways from regularity—first, the PPh₃ ligands are splayed back away from each other (P−Cu−P = 129.07(6), 128.43-(6)°) and the Cu−N distance is about 0.25 Å shorter than the Cu−P distances (Table 2). Therefore, the immediate coordination environment of the copper atom has approximate C_{2v} symmetry, with the 2-fold axis parallel to the Cu−N vector. The Cu−P distances, with an average value of 2.247[5] Å, are significantly shorter than those found in the tris-PPh₃ complex **3**, a further indication of the lesser degree of steric crowding in complex **4**.

Complex **5**, with formula [Cu(μ-sacch)(PPh₃)]₂, is a neutral dimeric complex in which the presence of only one PPh₃ ligand per saccharinate now permits the latter to approach the metal even more closely, forming a bridge between the two Cu(I) centers (Figure 3). The complex sits on a crystallographic 2-fold axis in space group $C2/c$. Each copper atom is three-coordinate, ligated by the P atom of one PPh₃ ligand, the carbonyl atom of one saccharinate, and the imido nitrogen atom of another sacch ligand. The planar environment at each metal is, however, severely distorted, with the phosphorus atom tilted toward the coordinated carbonyl oxygen (N(1)−Cu(1)−P(1) = 151.61(8)°,

O(1a)−Cu(1)−P(1), 100.30(6)°). This obviates steric crowding between the phenyl groups of triphenylphosphine, on one hand, and the ring and sulfonyl functions of the saccharinate. The sacch ligands bridge the two metal centers through the amidate-like system −N−C=O−, as has been observed previously for saccharinate bridging copper atoms[9] and also for metal−metal bonds.[8,22] In the present case, the Cu−N bond, at 1.933(2) Å, is stronger than the bond from Cu to the neutral carbonyl oxygen atom (Cu(1)−O(1a) = 2.130(2) Å). Taken together, the two copper atoms with their two bridges form an eight-membered ring with a boat conformation. The nonbonded Cu···Cu distance is 2.9978(8) Å. The coordination planes about the two copper centers are not parallel to each other but, rather, make an angle of 46.49(7)°, with the phosphorus atoms pushed away from each other, apparently to avoid steric crowding of the phenyl groups. In addition, the two ends of the molecule are not eclipsed; the torsion angle P(1)−Cu(1)···Cu(1a)−P(1a) has a value of ±73.63(6)°. (Both hands are present in the crystal.) The Cu−P distance, at 2.1884(9) Å, is shorter than those found in complexes **3**, and **4**, thus following the trend of shorter Cu−P distances with decreasing number of PPh₃ ligands about the metal.

Compound **6**, *trans*-[Cu(sacch)₂(NH₃)₄], has the six-coordinate structure and trans arrangement of the polyfunctional ligands found for a series of related first-row complexes of sacch and NH₃[23] and also for the analogous sacch/aqua complexes.[6a] Despite the relative stability of the other saccharinate complexes with the same topology, **6** is unstable and evolves spontaneously either in solution or in the solid to the dark blue color characteristic of complex **7**. Indeed, if reaction conditions are not carefully controlled, any of the Cu(I) complexes and the Cu(II) starting material **1** will yield the more stable product **7** upon reaction with NH₃. A drawing of the neutral molecule **6** is shown in Figure 4a. The copper atom sits on a crystallographic inversion center. The two sacch ligands are only weakly bound to copper (Cu(1)−N(1) = 2.508(12) Å). The obvious interpretation of this is in terms of the Jahn−Teller theorem, although we note that in the analogous complexes [M(sacch)₂(H₂O)₄]·2H₂O (M = Mn, Fe, Co, Ni, Zn, Cd) and [M(sacch)₂(NH₃)₄] (M = Mn, Co, Ni, Cd), the values of M−N(sacch) range from 2.1 to 2.3 Å. Complex **6** also has a shape distortion in the solid, as can be appreciated from Figure 4b, which shows a side-on view of one molecule. The saccharinate ligands are pitched out of a central plane of the coordination environment in a concerted fashion, so that the molecule retains its center of symmetry. The misdirected valence parameter, defined as the angle between the Cu−N vector and the external bisector of the C(1)−N(1)−S(1) angle, has a value of 14.5°. This sort of effect can be seen in systems in which highly stabilizing phenomena in the crystal, such as aggregate structures, predominate over the natural tendencies of individual molecules, but in the present case crystal effects likely meet little resistance from the weak and probably nonrigid Cu−N(sacch) bond.

Complex **7**, [Cu(sacch)(NH₃)₄](sacch)·H₂O, can be synthesized directly from CuCl₂·6H₂O and ammonia or, alternatively, by reaction of the aqua complex **1** with NH₃ or starting from any of the Cu(I) complexes **3**−**5**. It is also formed by evolution of **6**, with the latter either in solution or as a solid exposed to air. Figure 5 shows one complete formula unit of **7**, which

(21) The deviation of an average value, given in square brackets, is calculated as $\left[\dfrac{\sum_i (d_i - d)}{n(n-1)}\right]^{1/2}$ in which d_i is the ith of the n values being averaged and d is the average.

(22) Alfaro, N. M.; Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1992**, *31*, 2718−2723.

(23) (a) Pascual, I. Doctoral Thesis, University of Zaragoza, 1996. (b) Pascual, I. *Acta Crystallogr., Sect. C* **1995**, *C51*, 2028−2030.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Cu(sacch)(PPh₃)₃ (**3**), Cu(sacch)(PPh₃)₂·³/₄CHCl₃ (**4**·³/₄CHCl₃), [Cu(sacch)(PPh₃)]₂·CH₂Cl₂ (**5**·CH₂Cl₂), *trans*-[Cu(sacch)₂(NH₃)₄] (**6**), and [Cu(sacch)(NH₃)₄](sacch)·H₂O (**7**)[a]

|							
			Cu(sacch)(PPh₃)₃ (**3**)				
Cu(1)−O(1)	2.113(8)	Cu(1)−P(2)	2.373(3)	C(2)−O(1)	1.243(12)	N(1)−S(1)	1.610(10)
Cu(1)−P(1)	2.334(3)	Cu(1)−P(3)	2.335(4)	C(2)−N(1)	1.332(13)		
O(1)−Cu(1)−P(1)	113.8(2)	P(1)−Cu(1)−P(3)	111.12(13)	P(1)−Cu(1)−P(2)	117.33(13)	C(2)−O(1)−Cu(1)	129.8(8)
O(1)−Cu(1)−P(3)	103.4(2)	O(1)−Cu(1)−P(2)	90.2(2)	P(3)−Cu(1)−P(2)	118.18(13)		
			Cu(sacch)(PPh₃)₂·³/₄CHCl₃ (**4**·³/₄CHCl₃)				
Cu(1)−N(1)	1.976(5)	N(1)−C(1)	1.371(8)	Cu(2)−N(2)	2.012(5)	N(2)−C(44)	1.344(8)
Cu(1)−P(2)	2.2375(16)	N(1)−S(1)	1.621(5)	Cu(2)−P(4)	2.2441(16)	N(2)−S(2)	1.620(5)
Cu(1)−P(1)	2.2472(16)	C(1)−O(1)	1.231(7)	Cu(2)−P(3)	2.2591(17)	C(44)−O(4)	1.227(8)
N(1)−Cu(1)−P(2)	116.07(15)	C(1)−N(1)−Cu(1)	122.0(4)	N(2)−Cu(2)−P(3)	113.94(16)	C(44)−N(2)−Cu(2)	113.5(4)
N(1)−Cu(1)−P(1)	114.82(15)	S(1)−N(1)−Cu(1)	124.6(3)	P(4)−Cu(2)−P(3)	128.43(6)	S(2)−N(2)−Cu(2)	132.7(3)
P(2)−Cu(1)−P(1)	129.07(6)	O(1)−C(1)−N(1)	122.7(6)	C(44)−N(2)−S(2)	112.9(4)	O(4)−C(44)−N(2)	123.2(7)
C(1)−N(1)−S(1)	112.2(4)	N(2)−Cu(2)−P(4)	117.62(16)				
			[Cu(sacch)(PPh₃)]₂·CH₂Cl₂ (**5**·CH₂Cl₂)[b]				
Cu(1)−N(1)	1.933(2)	Cu(1)−P(1)	2.1884(9)	N(1)−C(1)	1.348(4)	C(1)−O(1)	1.240(3)
Cu(1)−O(1)#1	2.130(2)	Cu(1)−Cu(1)#1	2.9978(8)	N(1)−S(1)	1.644(2)		
N(1)−Cu(1)−O(1)#1	107.28(10)	N(1)−Cu(1)−Cu(1)#1	81.81(7)	C(1)−N(1)−S(1)	111.86(19)	O(1)−C(1)−N(1)	124.1(3)
N(1)−Cu(1)−P(1)	151.61(8)	O(1)#1-Cu(1)−Cu(1)#1	76.32(6)	C(1)−N(1)−Cu(1)	126.6(2)	C(1)−O(1)−Cu(1)#1	123.78(19)
O(1)#1−Cu(1)−P(1)	100.30(6)	P(1)−Cu(1)−Cu(1)#1	111.72(3)	S(1)−N(1)−Cu(1)	121.39(14)		
			trans-[Cu(sacch)₂(NH₃)₄] (**6**)[c]				
Cu(1)−N(2)	2.027(12)	Cu(1)−N(1)	2.508(12)	N(1)−S(1)	1.591(12)	C(1)−O(1)	1.259(17)
Cu(1)−N(3)	2.042(12)	N(1)−C(1)	1.365(19)				
N(2)−Cu(1)−N(3)	93.1(5)	N(3)−Cu(1)−N(1)#1	87.7(4)	C(1)−N(1)−S(1)	111.2(11)	S(1)−N(1)−Cu(1)	118.5(7)
N(2)−Cu(1)−N(3)#1	86.9(5)	N(2)−Cu(1)−N(1)	84.5(4)	C(1)−N(1)−Cu(1)	128.1(10)	O(1)−C(1)−N(1)	125.5(15)
N(2)−Cu(1)−N(1)#1	95.5(4)	N(3)−Cu(1)−N(1)	92.3(4)				
			[Cu(sacch)(NH₃)₄](sacch)·H₂O (**7**)				
Cu(1)−N(3)	2.017(2) *2.033(2)*	Cu(1)−O(5)	2.715(2) *2.705(3)*	N(1)−C(1)	1.363(3) *1.371(2)*	S(2)−N(2)	1.609(2) *1.635(4)*
Cu(1)−N(4)	2.030(3) *2.033(2)*	S(1)−O(2)	1.441(2) *1.458(5)*	C(1)−O(1)	1.228(3) *1.223(3)*	S(2)−C(14)	1.764(3) *1.748(5)*
Cu(1)−N(6)	2.030(3) *2.041(2)*	S(1)−O(3)	1.451(2) *1.457(5)*	S(2)−O(5)	1.441(2) *1.434(5)*	N(2)−C(8)	1.363(3) *1.362(2)*
Cu(1)−N(5)	2.035(3) *2.050(2)*	S(1)−N(1)	1.611(2) *1.596(5)*	S(2)−O(6)	1.448(2) *1.454(5)*	C(8)−O(4)	1.231(3) *1.238(3)*
Cu(1)−N(1)	2.328(2) *2.309(2)*						
N(3)−Cu(1)−N(4)	87.79(11) *87.16(9)*	N(4)−Cu(1)−N(1)	93.23(10) *93.80(8)*	N(5)−Cu(1)−O(5)	91.03(10) *90.45(9)*	S(2)−O(5)−Cu(1)	126.97(12) *125.6(2)*
N(3)−Cu(1)−N(6)	172.82(12) *172.49(11)*	N(6)−Cu(1)−N(1)	94.49(10) *94.90(8)*	N(1)−Cu(1)−O(5)	169.87(7) *169.96(9)*	O(5)−S(2)−O(6)	113.44(13) *113.8(3)*
N(4)−Cu(1)−N(6)	89.72(12) *90.04(9)*	N(5)−Cu(1)−N(1)	94.22(10) *93.87(9)*	C(1)−N(1)−S(1)	111.9(2) *112.09(19)*	O(5)−S(2)−N(2)	111.58(13) *111.4(3)*
N(3)−Cu(1)−N(5)	90.08(12) *90.07(8)*	N(3)−Cu(1)−O(5)	96.28(10) *96.82(9)*	C(1)−N(1)−Cu(1)	124.9(2) *124.32(12)*	O(6)−S(2)−N(2)	111.11(13) *109.7(3)*
N(4)−Cu(1)−N(5)	172.34(12) *171.94(11)*	N(4)−Cu(1)−O(5)	81.89(10) *82.38(9)*	S(1)−N(1)−Cu(1)	122.62(11) *122.76(17)*	C(8)−N(2)−S(2)	111.4(2) *111.3(2)*
N(6)−Cu(1)−N(5)	91.51(12) *91.76(9)*	N(6)−Cu(1)−O(5)	76.69(10) *75.89(8)*	O(1)−C(1)−N(1)	124.1(2) *124.60(19)*	O(4)−C(8)−N(2)	124.4(2) *124.45(19)*
N(3)−Cu(1)−N(1)	92.38(10) *92.24(9)*						

[a] For **7**, the distances and angles from the neutron diffraction analysis are given in italics. [b] Symmetry transformations used to generate equivalent atoms for **5**: (#1) −x, y, −z + ¹/₂. [c] Symmetry transformations used to generate equivalent atoms for **6**: (#1) −x, −y, −z.

corresponds to the crystallographic asymmetric unit and consists of the copper atom with its four NH₃ ligands, one imido-bound saccharinate (Cu−N$_{imido}$ = 2.328(2) Å from the X-ray analysis), one semicoordinated saccharinate (Cu−O$_{sulfonyl}$ = 2.715(2) Å), and one unligated molecule of water. The copper center has a distorted-octahedral environment, in which the N-bound saccharinate is closer to the metal than in complex **6** and the sulfonyl oxygen atom trans to this moiety is farther away. Table 2 presents selected distances and angles about the metal center. The presence of the unusual molecular entity [Cu(sacch)(NH₃)₄]-(sacch), with one saccharinate semicoordinated through a sulfonyl oxygen atom, is the result of the formation of a

supramolecular aggregate (Figure 6) consisting of two formula units of **7**, in which the "semicoordinated" saccharinate participates in three hydrogen bonds and one electrostatic interaction that approximates hydrogen bonding. The unligated water molecule is the donor in two hydrogen bonds that bind the aggregate, and it is the acceptor in a further electrostatic interaction which must also contribute significantly to stabilizing the overall structure. The aggregate structure sits across a crystallographic inversion center, and as shown in Figure 6, the extensive set of hydrogen bonds and purely electrostatic contacts binds the disparate and chemically unusual features of the molecular structure into a more symmetrical pattern in which
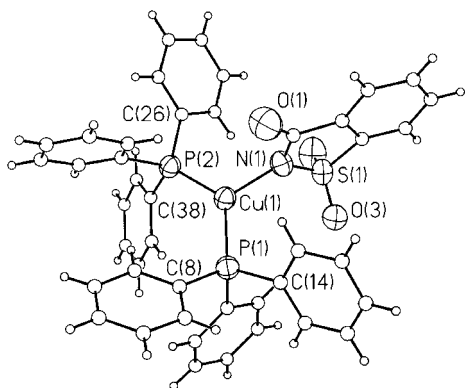
Figure 2. One molecule of Cu(sacch)(PPh₃)₂ (**4**), from the crystal structure of **4**·³/₄CHCl₃. Carbon and hydrogen atoms are shown as circles. Other atoms are represented by their 50% probability ellipsoids.
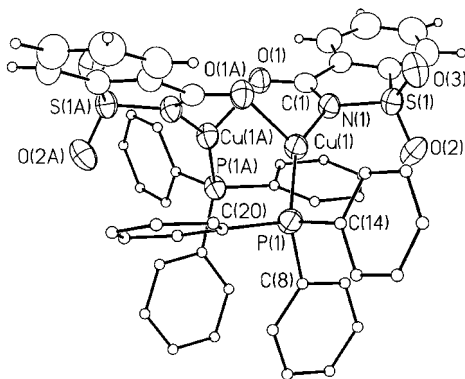

Figure 3. Drawing of [Cu(sacch)(PPh₃)]₂ (**5**), from the crystal structure of **5**·CH₂Cl₂. Phenyl group hydrogen atoms have been omitted. Phenyl carbon atoms and the hydrogen atoms of saccharinate are represented as circles. Other atoms are drawn as their 50% probability ellipsoids.
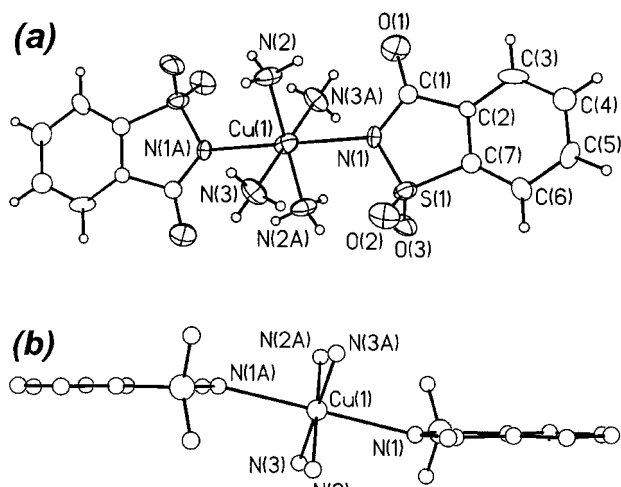

Figure 4. Structure of *trans*-[Cu(sacch)₂(NH₃)₄] (**6**): (a) thermal ellipsoid plot (50% probability), with the atom-labeling scheme indicated; (b) side-on view, showing the distortion caused by pitching of the saccharinate ligands.

none of the potential donor or acceptor atoms in electrostatic interactions remain unused.

The neutron structure determination of **7** serves the dual purpose of providing a clear distinction between NH₃ and H₂O in the structure and of supplying accurate parameters for the hydrogen-bonding pattern. Table 3 lists the H-bonds and purely electrostatic interactions, as characterized by both X-ray and neutron diffraction. We note that the N–H bond distances that emerge from the neutron structure determination are 0.16[2] Å
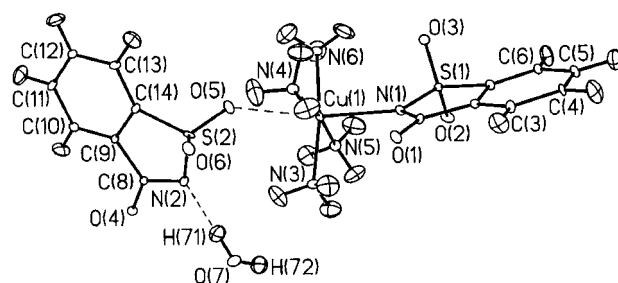
Figure 5. One asymmetric unit of [Cu(sacch)(NH₃)₄](sacch)·H₂O (**7**), from the neutron diffraction analysis. Atom S(1) was refined isotropically. All other atoms are represented by their 50% probability ellipsoids.
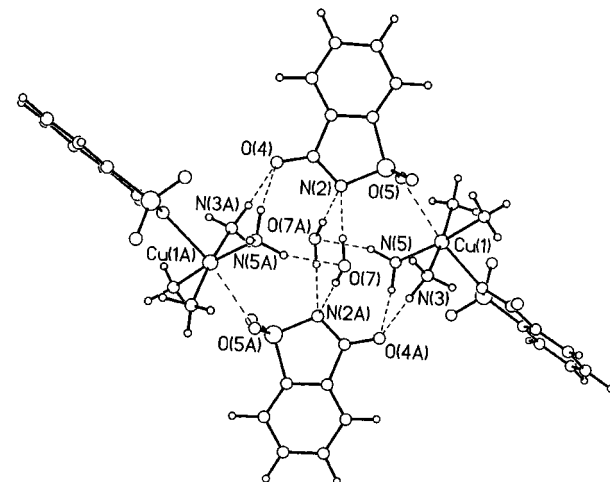
Figure 6. Drawing of the supramolecular aggregate formed by two asymmetric units of [Cu(sacch)(NH₃)₄](sacch)·H₂O (**7**), from the neutron diffraction analysis. Atoms with "A" appended to their names are related to their congeners by a crystallographic inversion center.

longer, on average, than those observed using X-ray diffraction; this is the expected difference between the internuclear distance observed by neutron diffraction and the difference between the centers of electron density observed using X-rays. The diminished libration at the lower temperature of the neutron structure determination is also expected to contribute to this difference, albeit to a lesser extent. The C–H bond distances also differ by 0.16[2] Å on average. Of the two O–H bonds in the water molecule, one is about 0.1 Å longer in the neutron diffraction results, and the other is essentially identical in the neutron and X-ray analyses; the latter is likely an artifact of an anomalously large value from the X-ray determination, which is more prone to inaccuracies in hydrogen atom positions.

IR Spectroscopy. Table 4 lists the most important IR bands for compounds **3**–**7**. The vibrational energies are well correlated with what is seen in the crystal structures. The C=O stretch of saccharinate is shifted to lower energy in compound **5** as compared to **4**, because in the former the carbonyl group is bound to one metal as part of the bridging system. The carbonyl stretch is found at even lower energy in **3**, in which sacch binds to copper exclusively through C=O. The other relevant IR bands—M–N, S=O₂, N–H, and O–H—are all consistent with the structures found by diffraction. It appears that the C=O bond distances tend to longer values as the carbonyl oxygen becomes more involved in coordination, although the statistical significance of slight differences in the relevant C=O and C–N bond distances does not permit rigorous discrimination among the values observed for **3**–**5**. We simply note that the C=O and C–N bonds tend to follow the expected trend[11] of longer C=

Table 3. Noncovalent Interactions within the Supramolecular Aggregate Formed by [Cu(sacch)(NH₃)₄](sacch)·H₂O (**7**)[a]

D−H···A	D···A, Å	D−H, Å	H···A, Å	D−H···A (deg)	acceptor coord
O(7) − H(71) ···N(2)	2.862(3)	0.85(4)	2.01(4)	176(4)	*x, y, z*
	2.869(3)	*0.972(6)*	*1.898(5)*	*177.3(4)*	
O(7) − H(72) ···N(2)	3.038(4)	0.97(6)	2.07(6)	174(4)	$1 − x, 1 − y, 1 − z$
	3.017(3)	*0.961(7)*	*2.056(5)*	*178.9(5)*	
N(5) − H(52) ···O(7)	3.142(4)	0.81(4)	2.36(4)	163(4)	$1 − x, 1 − y, 1 − z$
	3.107(3)	*1.022(6)*	*2.123(5)*	*160.9(4)*	
N(5) − H(53) ···O(4)	3.150(4)	0.92(5)	2.28(5)	157(4)	$1 − x, 1 − y, 1 − z$
	3.116(3)	*1.014(6)*	*2.173(5)*	*153.9(5)*	
N(3) − H(32) ···O(4)	2.915(3)	0.93(4)	2.00(4)	173(3)	$1 − x, 1 − y, 1 − z$
	2.911(3)	*1.016(5)*	*1.904(5)*	*170.3(4)*	

[a] Values from the neutron structure determination are given in italics.

Table 4. Principal IR Bands (cm^{-1}) for Compounds **3**−**7**

assign	**3**	**4**	**5**	**6**	**7**
C=O str	1612	1661	1637	1686−1612	1668−1587
M−N		394	397	402, 346	401
S=O	1153	1158, 1152	1168, 1157	1142, 1137, 1117	1154, 1119, 1054
N−H				3355	3351
O−H					3610

O and shorter C−N distances as the carbonyl becomes more involved in coordination (*i.e.,* on going from **4** to **5** to **3**).

Discussion

The most important result to emerge from this study of the Cu/sacch/{H₂O,PPh₃,NH₃} system is the manner in which saccharinate employs its polyfunctional nature to adapt to the steric needs of the complexes. Each of the three full coordination modes possible for sacch—bridging through the amidato-like system, coordinated through the imido nitrogen atom, and coordinated through the carbonyl oxygen—imposes distinct steric encumbrances on the complex formed; in each of the Cu(I) compounds saccharinate adopts the coordination mode appropriate to its surroundings. The Cu(I) compounds appear to participate in a complex equilibrium in solution, but we have found that the principal Cu(I) product isolated from a given reaction of **2** with PPh₃ possesses one fewer phosphine moiety than the number used in the preparation. Thus, for example, if a sacch:PPh₃ ratio of 1:4 is used in the preparation, the principal product isolated is complex **3**, Cu(sacch)(PPh₃)₃. Except for **6**, all of the compounds are stable enough to be handled without unusual precautions, and except for **6** all can be isolated—either from this reaction system or from parallel preparations—in yields ranging from moderate (about 50% for **5**) to nearly quantitative (complexes **4** and **7**). This signifies that the observed bonding modes are stable as well as interchangeable.

The semicoordination mode observed for one sacch moiety in **7**—that is, the formation of a long contact to copper through a sulfonyl oxygen atom—is unusual and requires explanation, especially in light of the fact that all of the other products evolve easily to **7** in the presence of the appropriate reagents. The formation of the aggregate structure (Figure 6) in the solid state must be the source of the special stability of **7**—crystals can even be kept under hard vacuum for periods of at least minutes without losing the unligated water. We do not expect that an isolated chemical entity such as that shown in Figure 5 has a significant lifetime in solution. We attempted to prepare complex **6**, *trans*-[Cu(sacch)₂(NH₃)₄], by various means beginning with **7**; we were unsuccessful in all cases, showing that dehydration of **7** and rearrangement of one saccharinate do not yield a more stable product. Although the aggregate does not possess any exceptionally strong hydrogen bonds, its overall stability is sufficient to make it a dominant feature of this chemistry.

Complex **6**, *trans*-[Cu(sacch)₂(NH₃)₄], was the original target of this chemistry. It was expected that its preparation would present no special problems, by analogy with the facile syntheses of the analogous aqua complexes of first-row transition elements, including copper, and of the ammine complexes of first-row elements other than copper. The instability of **6** can be attributed in large part to the availability of a highly stable alternative, **7**; however, the structure of **6** itself belies the presence of inherent physical instability. The [Cu(NH₃)₄]²⁺ moiety is chemically stable, but the weak bonding to saccharinate—enabled as one of the possible expressions of the Jahn−Teller effect and observed in the long bond distance and especially in the misdirected valence—undoubtedly confers a high degree of lability on the complex. It is noteworthy that although the loss of both sacch ligands from **6** would yield the stable entity [Cu-(NH₃)₄]²⁺, in the actual event the formation of **7** brings one of the sacch ligands closer to the copper center.

Scheme 1 summarizes the whole reaction system. The powder blue tetraaquabis(saccharinato)copper(II) dihydrate (**1**) turns deep green upon dehydration in an oven, presumably through loss of the waters of hydration, yielding **2**. This complex is the point of departure for the three Cu(I) complexes **3**−**5**, in which saccharinate is fully coordinated but with its bulk either nearer the center of the complex or farther away, depending on the steric permittivity of the remaining ligand arrangement. Any of the three Cu(I) complexes reacts with NH₃ in the absence of water to give the sky blue tetraamminobis(saccharinato)copper-(II) (**6**) which evolves rapidly to the royal blue complex **7** if water is not rigorously excluded. Except for the three colorless Cu(I) complexes, all of the compounds can be distinguished easily from each other by their colors.

The very stable complex **1**, with four aqua ligands in its central plane, gives way at the bottom of the reaction system to products **6** and **7**, in which the equatorial plane is populated by four NH₃ ligands. The identities of the auxiliary ligands H₂O in **1** and NH₃ in **7** have been established by single-crystal neutron diffraction analyses. (The neutron structure determination of **1** was reported previously.[24]) The neutron analysis was particularly useful for **7**, which has both ammine ligands and unligated water, although the identity of the water is clear from its role as acceptor in electrostatic interactions. The identity of the four auxiliary ligands NH₃ in complex **6** is inferred from their identity in complex **7**.

Conclusion

Saccharinate, as a ligand in coordination chemistry, has previously been observed to approach transition metal centers in four different ways, although coordination through the imido

(24) Cotton, F. A.; Falvello, L. R.; Murillo, C. A.; Schultz, A. J. *Eur. J. Solid State Inorg. Chem.* **1991**, *29,* 311−320.

nitrogen atom is by far the most commonly observed bonding mode. In the present study, the results with the $[Cu^I(sacch)_x(PPh_3)_y]$ complexes demonstrate that with a given transition metal and chemical environment, the coordination mode of saccharinate is highly adaptable to the steric requirements of the complex formed. The formation of the ammine complex **7** shows that the most basic atoms of saccharinate can be used in the formation of a structurally dominant supramolecular aggregate while its weakest electron donor, a sulfonyl oxygen atom, is directed at the transition metal.

Supporting Information Available: A Crystallographic Information File (CIF) containing crystal data, experimental parameters, and structural results for the X-ray analyses of **3**−**7** and for the neutron structure determination of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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