Inorganica Chimica Acta, 172 (1990) 185–190

The Characterization of Both the Coordinated and Non-coordinated Saccharinate Ion. The Syntheses and Crystal Structures of Aqua(2-formylpyridine thiosemicarbazonato)(saccharinato-*N*)copper(II) Hemihydrate and 2,2′-Bipyridyl-(2-formylpyridine thiosemicarbazonato)copper(II) Saccharinate Dihydrate

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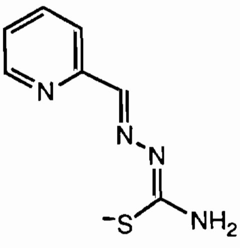
(Received December 1, 1989)

Abstract

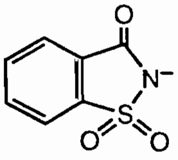
The preparation of the complex $[CuL(sacc)(H_2O)]\cdot 0.5H_2O$ (HL = 2-formylpyridine thiosemicarbazone, Hsacc = saccharin) from the reaction of Na(sacc) with $[\{CuL(CH_3COO)\}_2]$ is described. The complex $[CuL(bpy)](sacc)\cdot 2H_2O$ (bpy = 2,2′-bipyridyl) is obtained if the reaction is carried out in the presence of 2,2′-bipyridyl. The complexes have been characterized by a variety of physicochemical techniques and their crystal and molecular structures determined. Crystals of $[CuL(sacc)(H_2O)]\cdot 0.5H_2O$ are monoclinic, space group $P2_1/n$, with $a = 7.465(7)$, $b = 9.245(7)$, $c = 26.209(33)$ Å, $\beta = 97.18(9)°$ and $Z = 4$. Crystals of $[CuL(bpy)](sacc)\cdot 2H_2O$ are triclinic, space group $P\bar{1}$, $a = 9.243(1)$, $b = 12.393(1)$, $c = 13.323(1)$ Å, $\alpha = 75.511(5)$, $\beta = 67.751(5)$, $\gamma = 73.294(7)°$ and $Z = 2$. Both complexes contain five coordinate copper with three donor atoms (NNS) contributed by L, which forms a tricyclic ligating system. For $[CuL(sacc)(H_2O)]\cdot 0.5H_2O$ the coordination sphere is completed by a monodentate N-bound saccharinate ion and a more weakly bound water molecule giving a distorted square-pyramidal geometry. For the complex $[CuL(bpy)](sacc)\cdot 2H_2O$ the remaining coordination sites are occupied by two N atoms from 2,2′-bipyridyl, resulting in a geometry intermediate between square-pyramidal and trigonal-bipyramidal. The saccharinate ion is a non-coordinated anion.

Introduction

In an attempt to gain a better understanting of the antitumour properties of the copper(II) 2-formylpyridine thiosemicarbazone (HL) system, [1, 2] and to place its proposed mode of action [3] on a firmer chemical basis, we have been developing its chemistry. Although the parent compound $[\{CuL(CH_3COO)\}_2]$ is a dimer in the solid state, [4, 5] the active species *in vivo* is undoubtedly the monomeric cation $[CuL(H_2O)]^+$ [3]. It readily forms adducts with a range of N and S donor ligands e.g. $[CuL(bpy)]ClO_4$ (bpy = 2,2′-bipyridyl) [6], and its remarkable stability, in aqueous solution at low pH, allows the isolation of neutral HL ligand complexes such as $[\{Cu(HL)(SO_4)\}_2]$, [4], $[\{Cu(HL)(CF_3COO)\}_2](CF_3COO)_2$ and $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$ [7]. In this paper we explore its interaction with the biologically relevant anion, the saccharinate (sacc) ion.



L⁻



Sacc⁻

Saccharin (or *o*-sulphobenzoimide) itself is widely used as an artificial sweetener. A suggestion has been made that the importance of saccharin complexes lies in the potential use of saccharin as an antidote for metal poisoning [8]. Metal complexes of saccharin may also have relevance for an understanding of its human metabolism [9]. In binding to metal ions, it acts either as a monodentate anion, coordinating via the nitrogen or carbonyl oxygen atom, or as a bidentate ligand, using both donor atoms [10]. Most of the complexes that have been reported are binary hydrates, such as $[Cu(sacc)_2(H_2O)_4]\cdot 2H_2O$ [11], although exceptions are the ternary complexes, $[V(sacc)_2(py)_4]\cdot 2$solv (py = pyridine, solv = py or

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0020-1693/90/$3.50

tetrahydrofuran [12]. We now report that the CuL^+ species reacts with sodium saccharinate to yield the five coordinate complex $[CuL(sacc)(H_2O)]\cdot 0.5H_2O$, in which the saccharinate ion is an N-bound in-plane ligand. In contrast, in the presence of the chelate, 2,2′-bipyridyl, the reaction yields the complex $[CuL(bpy)](sacc)\cdot 2H_2O$, containing a non-coordinated saccharinate ion.

Experimental

Microanalyses, magnetic susceptibility, conductivity, IR, electronic and X-band ESR spectral measurements were carried out as previously described [6]. The ligand, HL, was synthesized following a published method [13], as was the complex $[\{CuL(CH_3COO)\}_2]$ [4]. Sodium saccharinate was purchased from Aldrich Chemical Co.

Synthesis of the Copper Complexes

$[CuL(sacc)(H_2O)]\cdot 0.5H_2O$

To a hot, filtered solution of $[\{CuL(CH_3COO)\}_2]$ (151 mg, 0.25 mmol) in water (75 cm^3) was added sodium saccharinate (213 mg, 1.04 mmol) in water (20 cm^3). The solution, after standing overnight, yielded dark green crystals of the product which were washed with water and air dried. Yield: 164 mg (73%). *Anal.* Found: C, 36.5; H, 3.1; N, 15.1. Calc. for $C_{14}H_{14}CuN_5O_{4.5}S_2$: C, 37.2; H, 3.1; N, 15.5%.

$[CuL(bpy)](sacc)\cdot 2H_2O$

To a hot, filtered solution of $[\{CuL(CH_3COO)\}_2]$ (300 mg, 0.50 mmol) and bpy (160 mg, 1.03 mmol) in ethanol (10 cm^3) was added sodium saccharinate (205 mg, 1.00 mmol) dissolved in water (5 cm^3). After several days dark green crystals of the product were obtained and washed with ethanol. Yield: 200 mg (65%). Since the compound readily loses H_2O the analytical data were obtained on an anhydrous sample prepared by drying the hydrate *in vacuo*. *Anal.* Found: C, 49.3; H, 3.2; N, 17.2. Calc. for $C_{24}H_{19}CuN_7O_3S_2$: C, 49.6; H, 3.3; N, 16.9%. For crystallographic work, freshly-prepared crystals were sealed in glass capillary tubes in the presence of mother liquor.

Crystal Structure of Aqua(2-formylpyridine thiosemicarbazonato)(saccharinato-N)copper(II) Hemihydrate, $[CuL(sacc)(H_2O)]\cdot 0.5H_2O$

Crystal data

$C_{14}H_{14}CuN_5O_{4.5}S_2$, $M = 452.0$, monoclinic, $a = 7.465(7)$, $b = 9.245(7)$, $c = 26.209(33)$ Å, $\beta = 97.18(9)$, $U = 1794.6$ Å^3 (by least-squares refinement of the angular settings of 25 reflections), space group $P2_1/n$, $Z = 4$, $D_c = 1.673$ g cm^{-3}, $F(000) = 912$, $\mu(Mo\ K\alpha) = 14.08$ cm^{-1}. Crystal size 0.10 × 0.26 × 0.63 mm.

Data collection and processing

Nicolet R3M diffractometer at 153 K, $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), θ range 2.0–22.5°, scan range 3.2°, scan speed 4.88°/min, 2533 reflections measured, data corrected for Lorentz and polarization effects, empirical absorption corrections applied.

Structure analysis and refinement

The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares refinement (SHELX-76). A difference electron density synthesis revealed all hydrogen atom positions and these were included in subsequent calculations; those on the pyridine and saccharinate rings and on C(6) were fixed with C–H = 1.08 Å. All non-hydrogen atoms were refined assuming anisotropic thermal motion but with the saccharinate phenyl ring being treated as a rigid group (C–C = 1.395, C–H = 1.08 Å). At convergence, values of R and R_w were both 0.054 for the 236 variables and 1372 reflections with $F^2 > 3\sigma(F^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, defined as $w = 1.7507/[\sigma^2(F) + 0.00104F^2]$. For Cu, atomic scattering factors were taken from the tabulations of Cromer and Mann [14], anomalous dispersion corrections were from Cromer and Liberman [15]. Final atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2.

Crystal Structure of 2,2′-Bipyridyl(2-formylpyridine thiosemicarbazonato)copper(II) Saccharinate Dihydrate $[CuL(bpy)](sacc)\cdot 2H_2O$

Crystal data

$C_{24}H_{23}CuN_7O_5S_2$, $M = 616.7$, triclinic, $a = 9.423(1)$, $b = 12.393(1)$, $c = 13.323(1)$ Å, $\alpha = 75.511(5)$, $\beta = 67.751(5)$, $\gamma = 73.294(7)°$, $U = 1361.65$ Å^3 (by least-squares refinement of the angular settings of 23 reflections), space group $P\bar{1}$, $Z = 2$, $D_c = 1.50$ g cm^{-3}, $D_o = 1.53$ g cm^{-3} (by flotation), $F(000) = 630$, $\mu(Cu\ K\alpha) = 28.12$ cm^{-1}. Dark green crystals in capillary tube; size 0.4 × 0.4 × 0.3 mm.

Data collection and processing

Enraf Nonius CAD-4 diffractometer, room temperature, Cu Kα radiation ($\lambda = 1.5418$ Å), θ range 2.0–75.0°, $\omega/2\theta$ scans of width 0.8°, five standard reflections monitored every 2 h, 5890 reflections measured. Data corrected for Lorentz and polarization effects, radiation decay (3%) and absorption (empirical azimuthal corrections, maximum value 1.2).

TABLE 1. Atomic coordinates ($\times 10^4$) for [CuL(sacc)(H_2O)]·$0.5H_2O$ with standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	3030(2)	3450(1)	669.1(0.4)
S(1)	1862(4)	1458(3)	249(1)
S(2)	3142(3)	1616(3)	1702(1)
O(1)	1861(8)	648(9)	1442(3)
O(2)	2478(11)	2634(9)	2052(3)
O(3)	7150(9)	2550(8)	1086(3)
O(10)	541(9)	4265(8)	1086(2)
O(11)	3896(18)	1957(12)	3325(5)
N(1)	4135(11)	5422(9)	820(3)
N(2)	2262(10)	4375(10)	7(3)
N(3)	1340(11)	3726(9)	−411(3)
N(4)	295(11)	1528(10)	−705(3)
N(5)	4247(11)	2446(9)	1281(3)
C(1)	5146(15)	5915(12)	1229(4)
C(2)	5730(16)	7359(15)	1295(4)
C(3)	5210(16)	8325(14)	894(5)
C(4)	4236(14)	7837(12)	456(4)
C(5)	3702(12)	6371(13)	426(4)
C(6)	2666(14)	5721(12)	−21(4)
C(7)	1107(13)	2317(12)	−320(4)
C(8)	6090(14)	2070(11)	1347(4)
C(9)	6481(6)	1055(7)	1776(2)
C(10)	8148(6)	453(7)	1963(2)
C(11)	8289(6)	−480(7)	2384(2)
C(12)	6762(6)	−811(7)	2619(2)
C(13)	5095(6)	−208(7)	2432(2)
C(14)	4954(6)	725(7)	2011(2)

TABLE 2. Selected distances (Å) and angles (°) for [CuL(sacc)(H_2O)]·$0.5H_2O$ with standard deviations in parentheses

Cu–S(1)	2.264(3)	C(1)–C(2)	1.408(16)
Cu–O(10)	2.393(7)	C(2)–C(3)	1.397(17)
Cu–N(1)	2.020(8)	C(3)–C(4)	1.358(14)
Cu–N(2)	1.956(8)	C(4)–C(5)	1.411(15)
Cu–N(5)	1.974(8)	C(5)–C(6)	1.451(14)
S(1)–C(7)	1.721(10)	S(2)–O(1)	1.420(7)
N(1)–C(1)	1.314(13)	S(2)–O(2)	1.444(8)
N(1)–C(5)	1.362(12)	S(2)–N(5)	1.648(8)
N(2)–N(3)	1.358(10)	S(2)–C(14)	1.700(5)
N(2)–C(6)	1.285(13)	O(3)–C(8)	1.195(11)
N(3)–C(7)	1.340(13)	N(5)–C(8)	1.408(12)
N(4)–C(7)	1.327(12)	C(8)–C(9)	1.465(11)
O(3)...O(10) [a]	2.986	N(4)...O(11) [d]	2.976
O(10)...O(11) [b]	2.931	N(4)...S(1) [e]	3.481
O(10)...N(3) [c]	2.816		
S(1)–Cu–O(10)	101.8(2)	N(1)–C(5)–C(4)	122.6(9)
S(1)–Cu–N(1)	162.3(2)	N(1)–C(5)–C(6)	113.4(10)
S(1)–Cu–N(2)	82.6(3)	C(4)–C(5)–C(6)	124.1(10)
S(1)–Cu–N(5)	97.1(3)	N(2)–C(6)–C(5)	117.5(10)
O(10)–Cu–N(1)	87.0(3)	S(1)–C(7)–N(3)	124.6(8)
O(10)–Cu–N(2)	96.3(3)	S(1)–C(7)–N(4)	118.2(8)
O(10)–Cu–N(5)	94.7(3)	N(3)–C(7)–N(4)	117.2(9)
N(1)–Cu–N(2)	81.2(3)	O(1)–S(2)–O(2)	116.8(5)
N(1)–Cu–N(5)	97.5(3)	O(1)–S(2)–N(5)	109.6(4)
N(2)–Cu–N(5)	168.9(3)	O(1)–S(2)–C(14)	111.7(4)
Cu–S(1)–C(7)	96.3(4)	O(2)–S(2)–N(5)	111.2(5)
Cu–N(1)–C(1)	130.7(8)	O(2)–S(2)–C(14)	109.3(4)
Cu–N(1)–C(5)	112.4(6)	N(5)–S(2)–C(14)	96.2(4)
C(1)–N(1)–C(5)	116.9(9)	Cu–N(5)–S(2)	123.0(4)
Cu–N(2)–N(3)	125.9(7)	Cu–N(5)–C(8)	124.0(6)
Cu–N(2)–C(6)	115.4(7)	S(2)–N(5)–C(8)	111.5(7)
N(3)–N(2)–C(6)	118.8(9)	O(3)–C(8)–N(5)	123.0(9)
N(2)–N(3)–C(7)	110.4(8)	O(3)–C(8)–C(9)	126.5(9)
N(1)–C(1)–C(2)	124.5(11)	N(5)–C(8)–C(9)	110.5(8)
C(1)–C(2)–C(3)	117.4(11)	C(8)–C(9)–C(10)	127.5(4)
C(2)–C(3)–C(4)	119.6(11)	C(8)–C(9)–C(14)	112.5(4)
C(3)–C(4)–C(5)	118.9(11)	S(2)–C(14)–C(9)	109.3(2)
		S(2)–C(14)–C(13)	130.7(2)

[a] Atom at $(1 + x, y, z)$. [b] Atom at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$. [c] Atom at $(-x, 1 - y, -z)$. [d] Atom at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$. [e] Atom at $(-x, -y, -z)$.

Structure analysis and refinement

The structure was solved by direct methods (MULTAN) and subsequent Fourier syntheses. Refinement was by full matrix least-squares (SHELX-76) assuming anisotropic thermal motion for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions for the L, bpy and sacc moieties, except for the amino hydrogens on N(4) of L, and the water hydrogens, which were found from difference syntheses. Hydrogen atoms were not refined. At convergence R and R_w were 0.0551 and 0.0655 respectively for the 352 variables, and 4846 reflections with $F^2 > 3\sigma(F^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1.975/[\sigma^2(F) + 0.00486F^2]$. Atomic scattering factors were as for [CuL(sacc)(H_2O)]·$0.5H_2O$. Final coordinates of non-hydrogen atoms are given in Table 3 and selected bond lengths and angles in Table 4.

Results and Discussion

The complex [CuL(sacc)(H_2O)]·$0.5H_2O$ was prepared from the reaction of sodium saccharinate with [{CuL(CH_3COO)}$_2$] whereas if the reaction was carried out in the presence of 2,2′-bipyridyl the product was [CuL(bpy)](sacc)·$2H_2O$. Physicochemical data for the complexes are given in Table 5. The molar conductivity for [CuL(sacc)(H_2O)]·$0.5H_2O$ falls well below the value expected for a 1:1 electrolyte [16] pointing to saccharinate coordination. In contrast, the value for [CuL(bpy)](sacc)·$2H_2O$ indicates the ionic nature of the complex consistent with a non-coordinated anion. Magnetic and ESR data are normal for copper(II) centres. The electronic spectra exhibit a strong band at *c.* 400 nm which is assigned to a S → Cu(II) ligand to metal charge transfer absorption [4, 6, 7] and is typical of Cu(II)–L com-

TABLE 3. Atomic coordinates (×10^4) for [CuL(bpy)](sacc)·2H_2O with standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	117(1)	3075(1)	5985(1)
S(1)	−1523(1)	3435(1)	4994(1)
S(2)	6423(1)	3519(1)	1761(1)
N(1)	1738(3)	3286(2)	6552(2)
N(2)	1542(3)	3678(2)	4594(2)
N(3)	1276(3)	3939(2)	3619(2)
N(4)	−515(4)	4029(3)	2829(2)
N(5)	8204(4)	3287(3)	921(3)
N(6)	−1435(3)	2556(2)	7409(2)
N(7)	898(4)	1209(2)	6128(2)
O(1)	6369(3)	3738(3)	2786(2)
O(2)	5358(4)	4371(3)	1252(3)
O(3)	9984(4)	1780(4)	133(3)
O(4)	2414(7)	4308(5)	866(3)
O(5)	2464(5)	1987(4)	685(4)
C(1)	1769(5)	3120(3)	7573(3)
C(2)	3042(5)	3229(4)	7793(4)
C(3)	4301(6)	3513(4)	6942(4)
C(4)	4310(5)	3667(3)	5876(4)
C(5)	2991(4)	3570(3)	5714(3)
C(6)	2841(4)	3799(3)	4626(3)
C(7)	−145(4)	3827(2)	3745(2)
C(8)	8665(5)	2195(4)	733(3)
C(9)	7448(4)	1507(3)	1326(3)
C(10)	7525(6)	375(4)	1307(4)
C(11)	6208(6)	−48(3)	1871(4)
C(12)	4798(6)	629(4)	2447(4)
C(13)	4715(5)	1762(3)	2487(3)
C(14)	6061(4)	2165(3)	1922(3)
C(15)	−2540(4)	3290(3)	8046(3)
C(16)	−3745(4)	2946(4)	8953(3)
C(17)	−3786(5)	1796(4)	9202(3)
C(18)	−2653(5)	1028(4)	8565(3)
C(19)	−1467(4)	1443(3)	7657(2)
C(20)	−194(4)	686(3)	6939(3)
C(21)	−67(6)	−482(3)	7079(4)
C(22)	1198(8)	−1113(3)	6376(4)
C(23)	2330(8)	−588(4)	5562(5)
C(24)	2145(6)	589(4)	5458(4)

TABLE 4. Selected distances (Å) and angles (°) for [CuL(bpy)](sacc)·2H_2O with standard deviations in parentheses

Cu–S(1)	2.277(1)	C(1)–C(2)	1.387(5)
Cu–N(1)	2.042(3)	C(2)–C(3)	1.355(6)
Cu–N(2)	1.949(2)	C(3)–C(4)	1.382(6)
Cu–N(6)	1.995(2)	C(4)–C(5)	1.381(5)
Cu–N(7)	2.198(2)	C(5)–C(6)	1.459(4)
S(1)–C(7)	1.736(3)	S(2)–O(1)	1.438(3)
N(1)–C(1)	1.335(4)	S(2)–O(2)	1.459(3)
N(1)–C(5)	1.344(4)	S(2)–N(5)	1.616(3)
N(2)–N(3)	1.358(4)	S(2)–C(14)	1.753(3)
N(2)–C(6)	1.292(4)	O(3)–C(8)	1.238(4)
N(3)–C(7)	1.329(4)	N(5)–C(8)	1.354(5)
N(4)–C(7)	1.338(4)	C(8)–C(9)	1.485(5)
O(1)...N(4) [a]	3.082	O(4)...N(4)	3.035
O(2)...O(4)	3.032	O(4)...O(5)	2.932
O(3)...O(5)	2.794		
S(1)–Cu–N(1)	159.9(1)	C(4)–C(5)–C(6)	122.4(3)
S(1)–Cu–N(2)	83.5(1)	N(2)–C(6)–C(5)	115.9(3)
S(1)–Cu–N(6)	94.9(1)	S(1)–C(7)–N(3)	124.9(2)
S(1)–Cu–N(7)	101.4(1)	S(1)–C(7)–N(4)	118.6(2)
N(7)–Cu–N(1)	95.1(1)	N(3)–C(7)–N(4)	116.5(3)
N(7)–Cu–N(2)	105.4(1)	Cu–N(6)–C(15)	122.4(2)
N(7)–Cu–N(6)	78.1(1)	Cu–N(6)–C(19)	117.4(2)
N(1)–Cu–N(2)	81.2(1)	Cu–N(7)–C(20)	111.0(2)
N(1)–Cu–N(6)	99.6(1)	Cu–N(7)–C(24)	128.7(3)
N(2)–Cu–N(6)	176.3(1)	O(1)–S(2)–O(2)	114.6(2)
Cu–S(1)–C(7)	94.9(1)	O(1)–S(2)–N(5)	111.2(2)
Cu–N(1)–C(1)	130.6(2)	O(1)–S(2)–C(14)	110.6(2)
Cu–N(1)–C(5)	110.9(2)	O(2)–S(2)–N(5)	112.2(2)
C(1)–N(1)–C(5)	118.3(3)	O(2)–S(2)–C(14)	109.4(2)
Cu–N(2)–N(3)	124.7(2)	N(5)–S(2)–C(14)	97.6(2)
Cu–N(2)–C(6)	115.8(2)	S(2)–N(5)–C(8)	110.4(3)
N(3)–N(2)–C(6)	119.4(3)	O(3)–C(8)–N(5)	124.2(4)
N(2)–N(3)–C(7)	111.4(2)	O(3)–C(8)–C(9)	121.7(4)
N(1)–C(1)–C(2)	122.3(3)	N(5)–C(8)–C(9)	114.1(3)
C(1)–C(2)–C(3)	118.9(4)	C(8)–C(9)–C(10)	129.0(3)
C(2)–C(3)–C(4)	119.9(4)	C(8)–C(9)–C(14)	111.0(3)
C(3)–C(4)–C(5)	118.3(4)	S(2)–C(14)–C(9)	106.7(2)
N(1)–C(5)–C(4)	122.3(4)	S(2)–C(14)–C(13)	130.2(3)
N(1)–C(5)–C(6)	115.3(3)		

[a] Atom at (1 + *x*, *y*, *z*).

TABLE 5. Physicochemical data for the complexes

	[CuL(sacc)(H_2O)]·0.5H_2O	[CuL(bpy)](sacc)·2H_2O
Λ (S cm^2 mol^{-1})	23[a]	74[b]
μ_{eff} (BM)[c]	1.80	1.81
ESR [d]		
$g_\perp$	2.048[e]	2.051[f]
$g_\parallel$	2.190	2.179
$A_\parallel$ (cm^{-1})		188 × 10^{-4}
λ_{max} (nm)[g]		
S → Cu	413	395
d–d	609	630, 870

[a] In Me_2SO (1:1 range 50–70 S cm^2 mol^{-1}). [b] In dimethylformamide (dmf) (1:1 range 60–80 S cm^2 mol^{-1}). [c] At 293 K [d] At 110 K. [e] Powder. [f] In frozen dmf. [g] Nujol mull transmittance.

plexes. The weaker d–d bands, observed at longer wavelengths, indicate that the coordination environment around the copper atom in each complex is different. In the case of [CuL(sacc)(H_2O)]·0.5H_2O, the one band at 609 nm is consistent with a distorted square-pyramidal geometry similar to that found in [{CuL(CH_3COO)}$_2$] (λ_{max} 640 nm) [4]. On the other hand, [CuL(bpy)](sacc)·2H_2O shows two d–d bands at 630 and 870 nm which, when compared with the values of 650 and 860 nm found for [CuL(bpy)]ClO_4, indicate the same copper stereochemistry in each case, namely a geometry intermediate between square pyramidal and trigonal bipyramidal [6].

Crystal Structures of [CuL(sacc)(H₂O)]·0.5H₂O and [CuL(bpy)](sacc)·2H₂O

Thermal ellipsoid drawings of the two structures, indicating the atom numbering schemes are depicted in Figs. 1 and 2. Bond lengths and angles are given in Tables 2 and 4. Both complexes crystallize as five-coordinate monomeric species. As indicated from the physicochemical results, however, the coordination geometries around the copper(II) atoms differ, and the saccharinate is bound to the metal in [CuL(sacc)(H_2O)]·0.5H_2O, but not in [CuL(bpy)](sacc)·2H_2O.

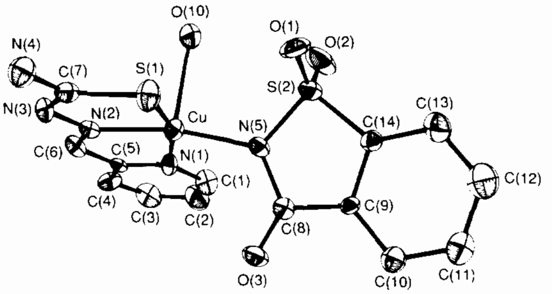

Fig. 1. The structure of the complex [CuL(sacc)(H_2O)] showing the numbering system used. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level.

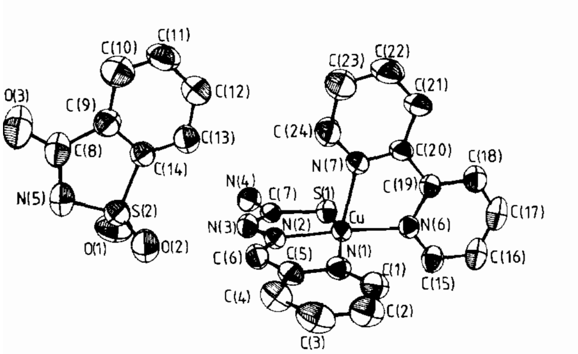

Fig. 2. The structure of the [CuL(bpy)]$^+$ cation and saccharinate anion, in the complex [CuL(bpy)](sacc)·2H_2O, showing the numbering system used.

In the first complex, [CuL(sacc)(H_2O)]·0.5H_2O, the copper atom adopts a distorted square-pyramidal geometry with the donor atoms being the pyridine nitrogen N(1), the imine nitrogen N(2) and the sulphur S(1) from the tridentate 2-formylpyridine thiosemicarbazonato ligand, the nitrogen N(5) from the saccharinato ion, and an oxygen O(10) from a water molecule. This latter ligand occupies the fifth apical position and, as is typical for such five-coordinate complexes [17], is more weakly bound [Cu–O(10) 2.393(7) Å]. The plane of best fit through the in-plane donor atoms shows the copper to be displaced out of the mean plane by 0.176(1) Å towards the apical oxygen, O(10). The closest sixth contact to the copper is that of the carbonyl oxygen, O(3), of the saccharinate. The distance of 3.24 Å is not considered a significant bonding contact although it may hinder the approach of another ligand. The saccharinate, as expected [8, 10, 12], is essentially planar, with the largest deviation from the plane of best fit being 0.016(6) Å. This plane makes an angle of 72° with the plane through the 2-formylpyridine thiosemicarbazonato ligand. The geometry of the Cu–L chromophore for this complex (and the second complex [CuL(bpy)](sacc)·2H_2O) is typical for such complexes [4, 6, 7] and will not be discussed further. The bonding parameters of the Cu(II)–saccharinate moiety in [CuL(sacc)(H_2O)]·0.5H_2O can be compared with those found for the six coordinate, tetragonal complex, [Cu(sacc)$_2$(H_2O)$_4$]·2H_2O [11]. The Cu–N(5) bond length at 1.974(8) Å in the former complex is significantly shorter than the value of 2.061(2) Å observed in the latter. This, in combination with a larger Cu–N(5)–S(2) bond angle (123.0(4) cf. 120.6(1)°) allows the carbonyl oxygen, O(3), of the saccharinate to make a closer contact with the copper atom in the five coordinate complex. (3.241 cf. 3.379 Å). Whereas there are differences in the geometries of the two coordinated saccharinates between the two complexes, the different coordination spheres and the different hydrogen bonding schemes mean they cannot easily be rationalized. For instance, the structure of [Cu(sacc)$_2$(H_2O)$_4$]·2H_2O shows that the saccharinate carbonyl oxygen, O(3), makes the hydrogen bonding contacts with water molecules (O(3)....O 2.604 and 2.810 Å) whereas in [CuL(sacc)(H_2O)]·0.5H_2O there is only one weaker interaction (O(3)....O(10) 2.986 Å) with a hydrogen of a coordinated water on a different copper centre. The coordinated water molecule also makes a hydrogen bond contact with the lattice water H_2O(11) (O(10)....O(11) 2.931 Å) and an intermolecular contact with the 2-formylpyridine thiosemicarbazonato N(3) of a second molecule (O(10).... N(3) 2.816 Å). The terminal N(4) hydrogens on L participate in two hydrogen bonds. One is with the lattice water H_2O(11) (O(11)....N(4) 2.976 Å) whereas the other is an intermolecular N–H....S interaction. The N(4)....S(1) distance is 3.481 Å which lies at the upper limit of the normal observed range (3.39 ± 0.12 Å) for such hydrogen bonds [18].

For the second complex reported in this paper, [CuL(bpy)](sacc)·$2H_2O$, the geometry around the copper is remarkably similar to that found for [CuL(bpy)](ClO_4) [6], and can be described as intermediate between square pyramidal and trigonal bipyramidal. Again the ligand, L, furnishes three donor atoms, N(1), N(2) and S(1) with the 2,2′-bipyridyl completing the coordination sphere with the nitrogens N(6) and N(7). It is clear that the geometry of the $[CuL(bpy)]^+$ cation is determined by the steric packing requirements of the L and bpy ligands. The anion (saccharinate or perchlorate) simply occupies a space in the lattice.

The saccharinate ion is planar, as is indicated by the maximum deviation (0.041 Å) of any atom from the mean plane of the ring atoms. The anion is hydrogen bonded to the two lattice waters via the sulphonyl oxygen O(2) (O(2)...O(4) 3.032 Å) and the carbonyl oxygen O(3) (O(3)...O(5) 2.794 Å), and to N(4) of the ligand L via the second sulphonyl oxygen O(1) (O(1)...N(4) 3.082 Å). The ligand L is also hydrogen bonded, through N(4), to one of the lattice waters (N(4)...O(4) 3.035 Å). Thus as in [CuL)sacc)(H_2O)]·$0.5H_2O$ both hydrogens on the terminal amino nitrogen, N(4), of L are used in hydrogen bonding.

Whereas there are significant differences between bond lengths in the saccharinates in [CuL(bpy)](sacc)·$2H_2O$ and [CuL(sacc)(H_2O)]·$0.5H_2O$ these must in part arise from the different hydrogen bonding schemes as well as differences from N atom coordination. For instance the N(5)–S(2) distance, at 1.616(3) Å, in the non-coordinated saccharinate compound is shorter than the analogous bond in the coordinated saccharinate complex (N(5)–S(2) 1.648(8) Å). However this difference (0.032 Å) is less than that found (0.054 Å) between the N–S distances in lead(II) disaccharinate monohydrate, where the two anions are both coordinated but crystallographically independent [10].

Conclusions

The fact that, from aqueous solution, the compound ({CuL(CH_3COO)}$_2$] forms an adduct with the saccharinate ion (which acts as an N-bound monodentate ligand) supports the idea [3] that *in vivo* the active form of the acetate is 'CuL^+'. The 'CuL(sacc)' chromophore serves as a model for intracellular adducts, of the type CuL^+–protein, in which CuL^+ is postulated to complex with amino acid side chains of proteins such as human haemoglobin [3]. However, in the presence of a chelate ligand (2,2′-bipyridyl) monodentate adduct formation is prevented, and the saccharinate remains non-coordinated.

Acknowledgements

We thank the New Zealand University Grants Committee for support and Dr W. T. Robinson (University of Canterbury) for the collection of an X-ray crystallographic data set.

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