*Inorganica Chimica Acta, 72 (1983) 21–27

X-ray Crystal Structures of Metal–Saccharin Complexes of General Formula $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$, where M = Fe(II), Co(II), Ni(II) and Cu(II)

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Received November 16, 1982

The crystal and molecular structures for the series of complexes, $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$ (M = Fe, Co, Ni and Cu) have been determined by single-crystal X-ray diffraction methods. The compounds crystallize in the monoclinic space group $P2_1/c$ *with lattice parameters:* $a = 7.929$, $b = 16.140$, $c = 7.738$ *Å and* $\beta = 99.77°$ *(iron complex),* $a = 7.908$, $b = 16.136$, $c = 7.688$ *Å and* $\beta = 99.60°$ *(cobalt complex),* $a = 7.918$, $b = 16.139$, $c = 7.651$ *Å and* $\beta = 99.94°$ *(nickel complex), and* $a = 8.384$, $b = 16.327$, $c = 7.327$ *Å and* $\beta = 101.08°$ *(copper complex). Full-matrix least-squares refinement has given* R *values of 0.040, 0.029, 0.032 and 0.034 based on 1600, 2556, 2449 and 1339 independent diffractometer data for the iron, cobalt, nickel and copper complexes respectively. The structural parameters in the series are compared and discussed in detail. The hydrogen bonding system in the copper complex is found to be significantly different from that in the other three compounds which form an isostructural series.*

Introduction

Metal complexes of *o*-sulphobenzoimide, commonly known as saccharin, ($C_7H_5NO_3S$, Hsac), are interesting because of their potential effectiveness in biological systems. Studies on these complexes have been very limited in the past, and the few reports [1–4] that are available lack any structural work. Very recently, we have described [5, 6] the syntheses, IR spectra and thermogravimetric analyses of saccharin complexes of some divalent transition metal ions. These complexes have the general formula $[M(sac)_2(H_2O)_4]\cdot 2H_2O$ where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). A brief account of the X-ray structure determination of the copper complex has been published [7]. In the present paper we describe the full details of the crystal structure analyses of the iron, cobalt, nickel and copper complexes. Preliminary data on the corresponding manganese and zinc complexes indicate that these also belong to this structurally-similar series of compounds.

Experimental

Single crystals of all the complexes suitable for X-ray crystallography were obtained by recrystallization from water. The unit-cell parameters were determined by least-squares refinement of the setting angles for twenty-five reflections automatically centered on diffractometers {Nonius CAD4 for $[Fe(sac)_2(H_2O)_4]\cdot 2H_2O$ (FESAC) and $[Cu(sac)_2(H_2O)_4]\cdot 2H_2O$ (CUSAC), and Syntex $P2_1$ for $[Co(sac)_2(H_2O)_4]\cdot 2H_2O$ (COSAC) and $[Ni(sac)_2(H_2O)_4]\cdot 2H_2O$ (NISAC)}. Mo-K_α radiation (graphite monochromator, $\lambda = 0.71069$ Å) was used in all cases. Conditions for systematic absences (*h*0*l*) absent for *l* odd, and 0*k*0 absent for *k* odd) suggested that all the complexes belong to the monoclinic space group $P2_1/c$ (No. 14). The full crystal data and some details of data collection and structure analyses are summarized in Table I.

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0020-1693/83/$03.00

TABLE I. Crystal Data and Summary of Intensity Measurements and Structure Analyses for $[M(sac)_2(H_2O)_4]\cdot 2H_2O$.

Crystal data	M = Fe	M = Co	M = Ni	M = Cu
F.W.	528.37	531.37	531.15	535.99
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	7.929(1)[a]	7.908(2)	7.918(2)	8.384(2)
b/Å	16.140(2)	16.136(2)	16.139(3)	16.327(2)
c/Å	7.738(2)	7.688(1)	7.651(2)	7.327(2)
β/°	99.77(2)	99.60(2)	99.94(2)	101.08(2)
U/Å^3	975.8	967.2	963.0	984.8
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	2	2	2	2
Dc/gcm^{-3}	1.81	1.82	1.83	1.81
μ(MoKα)/cm^{-1}	9.8	12.0	12.9	13.4
F(000)	544	546	548	550
Data collection				
Diffractometer	Nonius CAD4	Syntex P2$_1$	Syntex P2$_1$	Nonius CAD4
Crystal size/mm	0.25 × 0.15 × 0.12	0.40 × 0.40 × 0.40	0.40 × 0.30 × 0.30	0.32 × 0.18 × 0.10
θmin, θmax/°	1.5, 27	1.5, 30	1.5, 30	1.5, 25
Scan mode	$\omega-2\theta$	ω	ω	$\omega-2\theta$
ω-scan range/°	(0.8 + tanθ)	2	2	(0.8 + tanθ)
No. of reflections measured	1939	2822	2816	1992
No. of observed reflections	1600	2555	2449	1339
Significance level	$I_o > 2\sigma(I_o)$	$I_o > 2\sigma(I_o)$	$I_o > 2\sigma(I_o)$	$I_o > 2\sigma(I_o)$
Structure solution and refinement				
Program system	SHELX [9]	MULTAN [10]	MULTAN [10]	SHELX [9]
No. of parameters	182	172	172	182
Final $R = \Sigma\Delta F/\Sigma Fo$	0.040	0.029	0.032	0.034
$R' = (\Sigma w\Delta F^2/\Sigma wF^2)^{1/2}$	0.058	0.035	0.032	0.041

[a] The estimated standard deviations are given in parentheses, in this and other tables throughout the paper.

Three-dimensional X-ray intensity data for FESAC and CUSAC were recorded on the CAD4 diffractometer at room temperature (20 °C) by procedures described earlier [8]. The data for COSAC and NISAC were collected on the SyntexP2$_1$ diffractometer at −130 °C. On both the instruments the scan speed was variable depending on the counting rate. The data were corrected for Lorentz and polarisation effects and variable measuring times. Empirical absorption corrections were applied to the data for COSAC and NISAC, the absorption curves being obtained by ψ-scan of 6 and 9 reflections respectively. The data for FESAC and CUSAC were not corrected for absorption. Of 1939, 2822, 2816 and 1992 intensities measured for FESAC, COSAC, NISAC and CUSAC respectively, 1600, 2555, 2449 and 1339 were considered observed $[I_o > 2\sigma(I_o)]$ and used in the structure analyses.

The structures were solved by the application of direct methods employing the programs SHELX [9] for FESAC and CUSAC, and MULTAN [10] for COSAC and NISAC. Routine refinement of the structures by full-matrix least-squares, first with isotropic and then anisotropic temperature factors for all the non-hydrogen atoms, finally converged at $R = 0.040$, 0.029, 0.032 and 0.034 for FESAC, COSAC, NISAC and CUSAC respectively. The hydrogen atoms, located from difference electron density syntheses, were also included in the refinement, their isotropic temperature factors being varied in FESAC and CUSAC but fixed in COSAC and NISAC. The final difference maps did not show any region of significant electron density. In the final stage of refinement, weights calculated from counting statistics were applied to each reflection. The calculations were performed on an ICL 2980 at Queen Mary College, University of London, a NOVA 1200 (Data General) at the University of Stuttgart, and an IBM 360/115 at the University of Engineering and Technology, Dacca. Neutral atom scattering factors were taken from several sources [11–13].

TABLE II. Fractional Atom Coordinates for $[M(sac)_2(H_2O)_4]\cdot 2H_2O$.

Atom	M	x	y	z
M	Fe	0	0	0
	Co	0	0	0
	Ni	0	0	0
	Cu	0	0	0
S	Fe	0.3497(1)	−0.0590(1)	0.2801(1)
	Co	0.3472(1)	−0.0583(1)	0.2797(1)
	Ni	0.3448(1)	−0.0572(1)	0.2780(1)
	Cu	0.3279(1)	−0.0548(1)	0.2830(1)
O(1)	Fe	0.0651(2)	−0.2168(1)	0.0450(2)
	Co	0.0600(2)	−0.2155(1)	0.0445(2)
	Ni	0.0540(1)	−0.2140(1)	0.0420(2)
	Cu	0.0208(3)	−0.2049(1)	0.0654(3)
O(2)	Fe	0.2908(2)	−0.0197(1)	0.4267(2)
	Co	0.2896(2)	−0.0190(1)	0.4286(2)
	Ni	0.2888(2)	−0.0185(1)	0.4288(2)
	Cu	0.2989(3)	−0.0121(1)	0.4452(3)
O(3)	Fe	0.4629(2)	−0.0114(1)	0.1927(3)
	Co	0.4614(2)	−0.0109(1)	0.1913(2)
	Ni	0.4584(2)	−0.0100(1)	0.1887(2)
	Cu	0.4261(3)	−0.0134(1)	0.1708(3)
O(4)	Fe	0.0922(2)	0.0967(1)	0.1716(2)
	Co	0.0967(2)	0.0945(1)	0.1678(2)
	Ni	0.1028(2)	0.0925(1)	0.1674(2)
	Cu	0.1123(3)	0.0881(2)	0.1542(4)
O(5)	Fe	−0.1745(3)	−0.0363(2)	0.1723(3)
	Co	−0.1722(2)	−0.0354(1)	0.1712(2)
	Ni	−0.1711(2)	−0.0320(1)	0.1696(2)
	Cu	−0.2000(4)	−0.0263(2)	0.2054(5)
O(6)	Fe	−0.0051(3)	−0.1128(2)	0.4916(3)
	Co	−0.0080(2)	−0.1126(2)	0.4929(2)
	Ni	−0.0095(2)	−0.1124(1)	0.4920(2)
	Cu	−0.0333(4)	−0.1260(2)	0.5159(5)
N	Fe	0.1848(2)	−0.0920(1)	0.1404(2)
	Co	0.1815(2)	−0.0906(1)	0.1402(2)
	Ni	0.1774(2)	−0.0892(1)	0.1373(2)
	Cu	0.1541(3)	−0.0843(2)	0.1520(3)
C(1)	Fe	0.1794(3)	−0.1762(1)	0.1373(3)
	Co	0.1750(2)	−0.1750(1)	0.1374(2)
	Ni	0.1698(2)	−0.1737(1)	0.1345(2)
	Cu	0.1404(4)	−0.1674(2)	0.1513(4)
C(2)	Fe	0.3264(3)	−0.2157(1)	0.2558(3)
	Co	0.3226(2)	−0.2150(1)	0.2550(2)
	Ni	0.3182(2)	−0.2138(1)	0.2526(2)
	Cu	0.2854(4)	−0.2094(2)	0.2599(4)
C(3)	Fe	0.3663(3)	−0.2989(2)	0.2835(3)
	Co	0.3602(2)	−0.2985(1)	0.2820(3)
	Ni	0.3557(3)	−0.2972(1)	0.2803(3)
	Cu	0.3168(4)	−0.2923(2)	0.2823(5)
C(4)	Fe	0.5166(3)	−0.3192(2)	0.3945(3)
	Co	0.5122(3)	−0.3193(1)	0.3938(3)
	Ni	0.5080(3)	−0.3181(1)	0.3919(3)
	Cu	0.4655(4)	−0.3166(2)	0.3831(5)
C(5)	Fe	0.6264(3)	−0.2585(2)	0.4784(3)
	Co	0.6221(2)	−0.2590(1)	0.4763(3)
	Ni	0.6191(3)	−0.2585(1)	0.4791(3)
	Cu	0.5802(4)	−0.2601(2)	0.4635(5)
C(6)	Fe	0.5862(3)	−0.1750(1)	0.4533(3)
	Co	0.5839(2)	−0.1749(1)	0.4524(3)
	Ni	0.5819(2)	−0.1744(1)	0.4499(3)
	Cu	0.5503(4)	−0.1769(2)	0.4459(5)
C(7)	Fe	0.4375(3)	−0.1564(1)	0.3424(3)
	Co	0.4339(2)	−0.1561(1)	0.3406(2)
	Ni	0.4310(2)	−0.1552(1)	0.3379(2)
	Cu	0.4026(4)	−0.1536(2)	0.3415(4)
H(3)	Fe	0.292(3)	−0.345(2)	0.220(3)
	Co	0.277(3)	−0.344(2)	0.221(4)
	Ni	0.275(3)	−0.340(2)	0.227(4)
	Cu	0.246(5)	−0.324(2)	0.240(5)
H(4)	Fe	0.554(3)	−0.379(2)	0.408(3)
	Co	0.550(3)	−0.376(2)	0.408(4)
	Ni	0.536(3)	−0.368(2)	0.403(4)
	Cu	0.490(5)	−0.369(3)	0.394(6)
H(5)	Fe	0.733(3)	−0.276(2)	0.556(3)
	Co	0.738(3)	−0.277(2)	0.545(4)
	Ni	0.723(3)	−0.277(2)	0.544(4)
	Cu	0.683(4)	−0.277(3)	0.528(5)
H(6)	Fe	0.673(3)	−0.134(2)	0.515(4)
	Co	0.652(3)	−0.131(2)	0.505(4)
	Ni	0.654(3)	−0.137(2)	0.504(4)
	Cu	0.618(5)	−0.144(3)	0.486(5)
H(41)	Fe	0.049(4)	0.095(2)	0.282(5)
	Co	0.069(4)	0.097(2)	0.265(5)
	Ni	0.075(4)	0.092(2)	0.265(5)
	Cu	0.064(7)	0.086(4)	0.228(8)
H(42)	Fe	0.047(4)	0.136(2)	0.119(4)
	Co	0.072(4)	0.142(2)	0.135(4)
	Ni	0.065(4)	0.135(2)	0.116(4)
	Cu	0.087(5)	0.129(3)	0.101(7)
H(51)	Fe	−0.150(4)	−0.069(3)	0.239(5)
	Co	−0.133(4)	−0.068(2)	0.273(4)
	Ni	−0.133(4)	−0.065(2)	0.266(4)
	Cu	−0.197(10)	−0.000(5)	0.267(12)
H(52)	Fe	−0.281(6)	−0.028(3)	0.165(6)
	Co	−0.268(4)	−0.029(2)	0.162(4)
	Ni	−0.270(4)	−0.026(2)	0.158(4)
	Cu	−0.298(9)	−0.034(4)	0.160(9)
H(61)	Fe	0.017(4)	−0.167(3)	0.439(4)
	Co	0.021(4)	−0.167(2)	0.505(4)
	Ni	0.022(4)	−0.164(2)	0.500(4)
	Cu	−0.010(5)	−0.175(3)	0.507(6)
H(62)	Fe	0.091(11)	−0.076(7)	0.454(12)
	Co	0.082(4)	−0.089(2)	0.490(4)
	Ni	0.075(4)	−0.089(2)	0.485(4)
	Cu	−0.069(8)	−0.121(5)	0.429(9)

Results and Discussion

The final atomic fractional coordinates for all the complexes are given in Table II. The interatomic distances and inter-bond angles are listed in Table III. The parameters related to the hydrogen bonds are given in Table IV. The thermal parameters, and lists

TABLE III. Bond Lengths (Å) and Angles (°) in $[M(sac)_2(H_2O)_4]\cdot 2H_2O$.

Bond lengths	FESAC	COSAC	NISAC	CUSAC
M–N	2.235(2)	2.200(1)	2.154(1)	2.061(2)
M–O(4)	2.099(2)	2.060(1)	2.042(1)	1.956(2)
M–O(5)	2.159(2)	2.124(2)	2.096(2)	2.489(3)
S–N	1.638(2)	1.634(1)	1.640(2)	1.655(3)
S–C(7)	1.753(2)	1.753(2)	1.752(2)	1.753(3)
S–O(2)	1.444(2)	1.447(1)	1.448(2)	1.439(2)
S–O(3)	1.435(2)	1.438(2)	1.438(2)	1.438(2)
C(1)–N	1.359(3)	1.364(2)	1.366(2)	1.362(4)
C(1)–O(1)	1.241(3)	1.244(2)	1.240(2)	1.238(4)
C(1)–C(2)	1.498(3)	1.499(2)	1.499(2)	1.487(4)
C(2)–C(3)	1.389(3)	1.387(2)	1.387(3)	1.383(4)
C(3)–C(4)	1.385(3)	1.395(3)	1.393(3)	1.379(5)
C(4)–C(5)	1.396(4)	1.385(3)	1.380(3)	1.380(5)
C(5–C(6)	1.391(3)	1.396(3)	1.394(3)	1.383(5)
C(6)–C(7)	1.393(3)	1.378(3)	1.380(3)	1.378(4)
C(7)–C(2)	1.393(3)	1.385(2)	1.384(3)	1.388(4)
Bond angles				
O(4)–M–O(5)	90.1(1)	91.2(1)	91.3(1)	94.0(1)
O(4)–M–N	93.3(1)	92.4(1)	91.6(1)	90.2(1)
O(5)–M–N	92.5(1)	92.8(1)	91.7(1)	90.3(1)
O(2)–S–O(3)	116.5(1)	116.5(1)	116.9(1)	116.8(1)
O(2)–S–N	109.5(1)	109.6(1)	109.6(1)	110.5(1)
O(2)–S–C(7)	110.1(1)	110.1(1)	109.9(1)	110.7(1)
O(3)–S–N	110.9(1)	110.9(1)	110.9(1)	110.0(1)
O(3)–S–C(7)	111.0(1)	110.9(1)	110.8(1)	110.8(1)
C(7)–S–N	97.2(1)	97.1(1)	97.0(1)	96.2(1)
M–N–S	119.3(1)	119.8(1)	119.7(1)	120.6(1)
M–N–C(1)	129.7(2)	129.5(1)	129.6(1)	128.3(1)
S–N–C(1)	110.9(1)	110.6(1)	110.7(1)	110.9(1)
O(1)–C(1)–N	123.8(2)	123.8(2)	123.9(2)	123.6(3)
O(1)–C(1)–C(2)	122.9(2)	122.8(2)	122.9(2)	122.9(3)
C(2)–C(1)–N	113.3(2)	113.4(2)	113.2(2)	113.4(3)
C(1)–C(2)–C(3)	129.8(2)	129.5(2)	129.4(2)	129.2(3)
C(1)–C(2)–C(7)	111.4(2)	111.1(2)	111.4(2)	111.5(3)
C(3)–C(2)–C(7)	118.8(2)	119.4(2)	119.2(2)	119.3(3)
C(2)–C(3)–C(4)	118.3(2)	117.9(2)	117.9(2)	118.5(3)
C(3)–C(4)–C(5)	121.7(2)	121.5(2)	121.8(2)	121.3(3)
C(4)–C(5)–C(6)	120.3(2)	121.1(2)	121.0(2)	121.2(3)
C(5)–C(6)–C(7)	116.9(2)	116.2(2)	116.2(2)	116.8(3)
C(2)–C(7)–C(6)	123.9(2)	123.9(2)	124.0(2)	122.9(3)
C(2)–C(7)–S	107.2(2)	107.6(1)	107.6(1)	108.0(2)
C(6)–C(7)–S	129.0(2)	128.5(1)	128.4(2)	129.1(3)

of observed and calculated structure factors, are available from the authors on request.

The unit-cell parameters (Table I) for the complexes are similar in general, but those for CUSAC show larger variations from the corresponding values for FESAC, COSAC and NISAC. At a first glance it would seem that all the four complexes are isostructural. A close structural similarity of the complexes was also inferred from the results of their IR spectra and thermal decomposition patterns

TABLE IV. Dimensions of the Hydrogen Bonds.

A–B···C	M	AC (A)	AB (A)	BC (A)	ABC (°)
O(4)–H(41)···O(6)^{I}	Fe	2.768	0.97	1.812	168
	Co	2.827	0.81	2.021	175
	Ni	2.847	0.82	2.039	170
	Cu	2.697	0.74	2.046	147
O(4)–H(42)···O(1)^{II}	Fe	2.723	0.81	1.924	169
	Co	2.709	0.81	1.986	148
	Ni	2.696	0.82	1.897	166
	Cu	2.604	0.79	1.843	162
O(5)–H(51)···O(6)^{III}	Fe	2.882	0.75	2.208	150
	Co	2.873	0.95	1.952	165
	Ni	2.883	0.92	1.987	165
O(5)–H(51)···O(2)^{I}	Cu	2.898	0.59	2.425	139
O(5)–H(52)···O(3)^{IV}	Fe	2.934	0.84	2.098	173
	Co	2.954	0.75	2.211	169
	Ni	2.984	0.78	2.219	167
	Cu	3.100	0.85	2.352	147
O(6)–H(61)···O(1)^{V}	Fe	2.822	0.89	1.947	167
	Co	2.840	0.91	1.938	173
	Ni	2.860	0.86	2.011	168
	Cu	2.810	0.83	2.017	161
O(6)–H(62)···O(2)^{III}	Fe	2.901	1.04	1.871	170
	Co	2.908	0.81	2.107	168
	Ni	2.917	0.78	2.143	172
O(6)–H(62)···O(5)^{III}	Cu	2.952	0.66	2.398	144

Key to symmetry: I −x, −y, 1 − z; II −x, −y, −z; III x, y, z; IV −1 + x, y, z; V x, −½ − y, ½ + z.

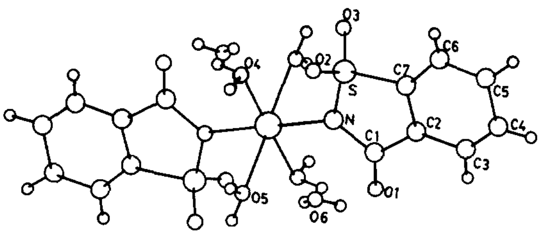

Fig. 1. *Structure of $[Cu(C_7H_4NO_3S)_2(H_2O)_4] \cdot 2H_2O$ showing the atom numbering in an asymmetric unit.

[5, 6]. Careful analysis of the crystallographic results, however, shows that it is only approximately correct to consider CUSAC as isostructural with the other three members of the series. This aspect is discussed in some detail later in the paper.

The complexes have the molecular formula $[M(C_7H_4NO_3S)_2(H_2O)_4]$ (M = metal), which take up two additional H_2O molecules (per mole complex) during the process of crystallization. The metal atoms are located on crystallographic inversion centres and have distorted octahedral geometry. Each metal is bonded to four H_2O molecules and two saccharinato ligands in *trans* positions. Contrary to earlier speculations about the metal-ligand bonding through the carbonyl or sulphonyl oxygen [4], we found in the present study that each saccharinato anion coordinates to the metal through its nitrogen. Figure 1 shows the structure of a single formula unit and indicates the atom numbering used.

The molecular geometry parameters, particularly those related to the coordination octahedra, present an interesting study. Comparison of the metal–nitrogen and metal–oxygen bond distances shows that all the M–N and M–O bonds, except Cu–O(5), are reduced systematically on going from FESAC to CUSAC. This general reduction of the metal to ligand bond lengths is consistent with the gradual

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*The figures are drawn from the copper complex. Packing diagrams would be the same for the four complexes. In the molecular structure, only the orientation of H(51) and H(62) is different (see text).

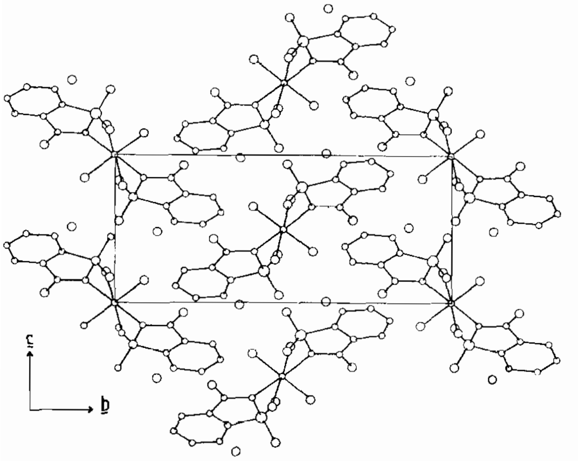

Fig. 2. The Crystal Structure projected down *a*.

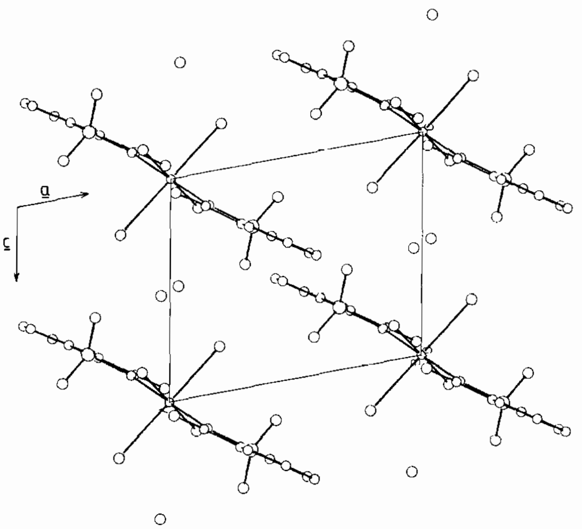

Fig. 3. The Crystal Structure projected down *b*.

decrease in the ionic radii due to the increase in the number of d-electrons from Fe^{+2} to Cu^{+2}.

Within each molecule the two unique M–O bonds are not the same, M–O(5) being longer than M–O(4). This difference is more pronounced in CUSAC than in the other complexes (0.533 *vs.* 0.054–0.064 Å), indicating somewhat weaker nature of the M–O(5) bond in the copper complex. The bond length data for each molecule also reveal some interesting features. For example, the difference in the metal–nitrogen and metal–oxygen bond lengths, Δ [MN–MO(4)], are 0.236, 0.140, 0.112 and 0.105 Å, *i.e.* progressively smaller in FESAC, COSAC, NISAC and CUSAC. This suggests that *either* the M–N bond gets relatively stronger, *or* the M–O(4) bond gets relatively weaker (*or* both) in the sequence FESAC, COSAC, NISAC, CUSAC. Similarly, the Δ[MN–MO(5)] values across the series are 0.076, 0.076, 0.058 and –0.428 Å, suggesting inter-dependence of the M–N and M–O(5) bonds to some extent. The fact that the Cu–O(5) bond is extremely long (2.489 Å) suggests immediately that this bond is much weaker than all other metal–oxygen bonds (1.956–2.159 Å). This explains the relatively low thermal stability of the copper complex [5].

The bond length data clearly indicate that the largest distortion of the octahedron occurs in CUSAC. In fact, large tetragonal distortion of the octahedron in Cu(II) complexes (d^9 system) is well known and generally explained in terms of the Jahn-Teller effect [14]. However, it is extremely difficult to find the exact contribution of this particular factor to the *total* distortion along the axial bonds. The so-called crystal packing forces, including inter-ligand interactions and hydrogen bonding effects, should also contribute to the observed distortions in our complexes. Certainly, the distortion in NISAC (d^8 system) could not arise from the Jahn-Teller effect, but other factors such as the differences in the donor atoms, their nature and environment, the hydrogen bonding effects and other inter-ligand interactions, could be responsible. The angular distortions of the octahedra are not large, the maximum deviation from an ideal O–M–O/N angle of 90° being only 4°.

Figures 2 and 3 show two views of the crystal structures projected down *a* and *b* respectively. It consists of $[M(C_7H_4NO_3S)_2(H_2O)_4]$ and H_2O molecules (two per mole complex) bound together by an extensive network of hydrogen bonds. As indicated by the results in Table IV, the hydrogen bonding systems are the same in FESAC, COSAC and NISAC, but significantly modified in CUSAC. Thus differences are observed in the hydrogen bonds involving H(51) and H(62) due to the different orientations of the O(5)–H(51) and O(6)–H(62) bonds in CUSAC relative to the corresponding bonds in the other three complexes. In CUSAC, these hydrogen atoms participate in the bonds O(5)–H(51)···O(2) (at –x, –y, 1 – z) and O(6)–H(62)···O(5) at x, y, z) whilst in FESAC, COSAC and NISAC, they form the bonds O(5)–H(51)···O(6) (at x, y, z) and O(6)–H(62)···O(2) (at x, y, z). These differences are significant and cannot be ignored in comparing crystal structures. It is therefore concluded that of the four compounds studied, only FESAC, COSAC and NISAC form an isostructural series. Although CUSAC has many similarities with these three, it is not isostructural in the strict sense.

The bond lengths and angles related to the saccharinato ligands in the four complexes are the same, within experimental error. Most of these values agree well with those found in free saccharin [15, 16], but there are also some noticeable differences. Thus, the ring angle at nitrogen is more acute (110.8 *vs.* 115.0°) in the complex than in free saccharin at the expense of the adjacent angles, N–S–C(7) (96.9 *vs.* 92.5°) and N–C(1)–C(2) (113.3 *vs.* 109.7°)*. These angular changes are obviously brought about by the coordination through nitrogen, but this does not affect the planarity of the ring systems. The sum of the internal angles (mean for the four complexes) remains 540° for the 5-membered ring and 720.0° for the 6-membered phenyl ring, both values corresponding to ideal planarity.

In respect of the ligand geometry, it is further noted that both the C–O and the S–O bond distances are slightly increased in the complexes compared with free saccharin. These differences are small (~0.024 Å in C–O and ~0.017 Å in S–O), but considered to be real since the variations, Δ(C–O) and Δ(S–O), are always positive. This is also consistent with the shifts to lower wavenumber of the ν(CO) and $\nu(SO_2)$ bands in the IR spectra of the complexes [5, 6]. The lenghening of the C–O and S–O bonds in the complexes can be attributed to the involvement of the carbonyl and sulphonyl oxygens in hydrogen bonding.

Acknowledgement

We thank the Bose Centre for Advanced Study and Research, University of Dacca, for financial support. The work has been carried under the Coordinated Research Program of Dacca University with Queen Mary College, London, and University of Stuttgart, Federal Republic of Germany.

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*The value used for comparison is the mean of the corresponding parameters in the four complexes; the value for free saccharin is the mean of two independent determinations [15, 16].