similar compounds (Golič & Lazarini, 1974*a*,*b*, 1975) and it was not necessary to invoke disorder of the Cl atoms to refine either their structures or the present structure. This fact, in contradiction to that found by Gómez-Beltrán *et al.* (1978*a*) in bis(tetramethylethylenediamine)Ni trichloroacetate, seems to indicate that disorder in the position of the Cl atoms in the trichloroacetate ion is far from being general behaviour.

Values of the angles between the best least-squares planes for various portions of the molecule and principal torsion angles, computed by *PARST* 5 (Nardelli, Musatti, Domiano & Andreetti, 1965), have been deposited.*

Most of the calculations were carried out on the HP-1000-F minicomputer of the Computing Center of the University of Oviedo.

The authors wish to thank Dr E. Gutiérrez-Puebla, Inorganic Chemistry Department , Universidad Complutense de Madrid, for measurement of the intensities.

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* See deposition footnote.

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Structural Studies of Tetraaquabis(saccharinato-*N*)zinc(II) Dihydrate, $[Zn(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$, and Tetraaquabis(saccharinato-*N*)cadmium(II) Dihydrate, $[Cd(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$*

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Abstract. Zn compound: $M_r = 537{\cdot}82$, monoclinic, $P2_1/c$, $a = 7{\cdot}939$ (2), $b = 16{\cdot}120$ (2), $c = 7{\cdot}691$ (2) Å, $\beta = 99{\cdot}87$ (2)°, $V = 969{\cdot}7$ Å^3, $Z = 2$, $D_m = 1{\cdot}83$, $D_x = 1{\cdot}84$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 14{\cdot}7$ cm^{-1}, $F(000) = 552$, $T = 294$ (2) K. Cd compound: $M_r = 584{\cdot}85$, monoclinic, $P2_1/c$, $a = 8{\cdot}036$ (2), $b = 16{\cdot}145$ (3), $c = 7{\cdot}870$ (1) Å, $\beta = 100{\cdot}24$ (1)°, $V = 1004{\cdot}8$ Å^3, $Z = 2$, $D_m = 1{\cdot}92$, $D_x = 1{\cdot}93$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 12{\cdot}4$ cm^{-1}, $F(000) = 588$, $T = 294$ (2) K. $R = 0{\cdot}028$ and $0{\cdot}025$ for 1581 and 1850 intensities, respectively. The isostructural pair of complexes have centrosymmetric *trans* octahedral geometry. Delocalization of the charge away from the N atom may explain the weakness of the *M*—N bond. The structures of the Cd^{II} and Zn^{II} compounds are compared with those involving Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} and trends in the metal–ligand *M*—N, *M*—OH$_2$ bond lengths are discussed.

Introduction. We have described the syntheses and properties of a series of complexes with general formula $[M(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) (Haider, Malik & Ahmed, 1981;

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* Saccharin is 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide.

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Haider & Malik, 1982) and reported the crystal structure analyses of the Fe, Co, Ni and Cu complexes (Ahmed, Habib, Haider, Malik & Hursthouse, 1981; Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983). While our work was in progress an independent structural report of the corresponding Mn complex appeared (Kamenar & Jovanovski, 1982). In the present paper, we describe the crystal structure determinations of the Zn and Cd derivatives and discuss the structural variations in all seven related complexes.

Experimental. Zn complex (ZNSAC) prepared as described earlier (Haider & Malik, 1982). Cd complex (CDSAC) prepared by reacting cadmium chloride with Na-saccharin in aqueous medium (Haider, Malik, Hursthouse & Wadsten, 1984). D_m by flotation. Crystals suitable for X-ray work obtained by recrystallization from water. Lattice parameters determined by least-squares refinement of setting angles for 25 reflections [$16 \le \theta(\text{Mo } K\alpha) \le 17°$], automatically centred on Enraf–Nonius CAD-4 diffractometer; intensity data recorded on same instrument, Mo $K\alpha$ radiation (graphite monochromator), following procedures described earlier (Hursthouse, Jones, Malik & Wilkinson, 1979). Semi-empirical absorption corrections applied to both data sets, using ψ-scan values for 3 reflections in each case. Merging equivalent reflections and omitting those with $F_o < 3\sigma(F_o)$ yielded 1581 (ZNSAC) and 1850 (CDSAC) unique data, which were used in structure analyses. Further experimental information is given in Table 1.

Structures solved by heavy-atom method and refined by least squares. All non-hydrogen atoms refined anisotropically, hydrogen atoms (located from difference maps) isotropically. In final stage of refinement empirical isotropic extinction parameter x varied in modified expression for calculated structure factor, $F_c' = F_c(1 - x F_c^2/\sin\theta)$, and weighting scheme based on $w = 1/[\sigma^2(F_o) + gF_o^2]$ applied. Refinement on F converged at $R = 0{\cdot}0281$ (ZNSAC) and 0·0246 (CDSAC), with $\Delta/\sigma < 0{\cdot}1$, absolute values of peaks and troughs in final difference maps $<0{\cdot}3\ \text{e Å}^{-3}$. Calculations performed on DEC VAX11/750 computer using *SHELX*76 (Sheldrick, 1976). Neutral-atom scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) for non-H and H atoms, respectively. Final atomic parameters and the bond lengths and angles involving the non-H atoms are given in Tables 2 and 3, respectively.*

Table 1. *Experimental details*

	ZNSAC	CDSAC
Crystal size (mm)	0·42 × 0·26 × 0·20	0·36 × 0·28 × 0·22
Transmission min., max.	0·801, 0·999	0·941, 0·999
$\theta_{\min}, \theta_{\max}$(°)	1·5, 25	1·5, 26
Reflection type (h −9–9, k 0–19, l 0–9)	$\pm h, k, l$	$\pm h, k, l$
Scan mode	ω–2θ	ω–2θ
ω-scan width (°)	(0·85 + 0·35tanθ)	(0·85 + 0·35tanθ)
Scan speed [(°) min^{-1}]	1·33–6·67	1·33–6·67
Total data	1924	2231
Total unique data	1704	1961
Total observed data	1581	1850
Number of variables	183	183
Parameter g in weighting scheme	0·0002	0·0004
Parameter x for extinction correction	14·9 (10) × 10^{-7}	10·7 (9) × 10^{-7}
$R = (\sum\Delta F/\sum F)$	0·0281	0·0246
$R_w = (\sum w\Delta F^2/\sum wF^2)^{1/2}$	0·0411	0·0392

Table 2. *Fractional atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
(*a*) ZNSAC				
Zn	0*	0*	0*	20·1
S	3474 (1)	−580 (1)	2808 (1)	16·1
O(1)	601 (2)	−2152 (1)	453 (2)	25
O(2)	2900 (2)	−189 (1)	4296 (2)	25
O(3)	4600 (2)	−105 (1)	1924 (2)	28
O(4)	997 (2)	942 (1)	1672 (2)	26
O(5)	−1744 (3)	−348 (1)	1742 (3)	38
O(6)	−69 (3)	−1127 (1)	4963 (2)	31
N	1816 (2)	−905 (1)	1405 (2)	18
C(1)	1748 (3)	−1750 (1)	1377 (3)	18
C(2)	3225 (3)	−2148 (1)	2559 (3)	18
C(3)	3603 (3)	−2980 (1)	2833 (3)	23
C(4)	5117 (3)	−3189 (1)	3950 (3)	27
C(5)	6213 (3)	−2586 (2)	4773 (3)	26
C(6)	5832 (3)	−1750 (1)	4529 (3)	22
C(7)	4336 (3)	−1558 (1)	3414 (3)	18
(*b*) CDSAC				
Cd	0*	0*	0*	20·5
S	3525 (1)	−605 (1)	2854 (1)	18·4
O(1)	760 (2)	−2193 (1)	489 (2)	28
O(2)	2930 (2)	−207 (1)	4274 (2)	28
O(3)	4636 (3)	−124 (1)	2005 (3)	31
O(4)	989 (2)	1066 (1)	1796 (2)	30
O(5)	−1821 (2)	−402 (2)	1866 (3)	47
O(6)	8 (2)	−1124 (2)	4956 (2)	34
N	1921 (2)	−944 (1)	1460 (2)	21
C(1)	1871 (2)	−1784 (1)	1418 (2)	20
C(2)	3328 (2)	−2175 (1)	2613 (2)	20
C(3)	3725 (3)	−3003 (1)	2888 (3)	27
C(4)	5205 (3)	−3205 (1)	4013 (3)	28
C(5)	6262 (3)	−2593 (1)	4856 (3)	29
C(6)	5862 (3)	−1762 (1)	4607 (3)	24
C(7)	4394 (2)	−1579 (1)	3481 (2)	19

* Invariant parameters.

Discussion. The structure of a single molecule of the Cd complex is shown in Fig. 1, which also indicates the atom labelling in the asymmetric unit. Each metal sits on a centre of symmetry and is bonded to four H_2O molecules and two monodentate $C_7H_4NO_3S$ ligands in a distorted octahedral environment. The carbonyl and sulphonyl oxygens of the $C_7H_4NO_3S$ ligand are not bound to the metal but are involved in the hydrogen-bonding network.

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* Lists of structure factors, anisotropic thermal parameters, coordinates, bond lengths and angles involving the saccharinato hydrogen atoms, hydrogen-bond dimensions and data related to least-squares plane and dihedral angle calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39313 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Molecular geometry parameters* (Å, °)

(*a*) ZNSAC			
O(4)–Zn	2·059 (4)	O(5)–Zn	2·159 (4)
N–Zn	2·200 (4)	O(2)–S	1·446 (3)
O(3)–S	1·434 (3)	N–S	1·639 (4)
C(7)–S	1·750 (4)	C(1)–O(1)	1·237 (3)
C(1)–N	1·363 (4)	C(2)–C(1)	1·500 (5)
C(3)–C(2)	1·382 (4)	C(7)–C(2)	1·385 (4)
C(4)–C(3)	1·394 (4)	C(5)–C(4)	1·383 (4)
C(6)–C(5)	1·388 (4)	C(7)–C(6)	1·375 (4)
O(5)–Zn–O(4)	91·3 (2)	N–Zn–O(4)	91·9 (2)
N–Zn–O(5)	87·6 (2)	O(3)–S–O(2)	116·7 (2)
N–S–O(2)	109·5 (2)	N–S–O(3)	110·7 (2)
C(7)–S–O(2)	110·1 (2)	C(7)–S–O(3)	111·1 (2)
C(7)–S–N	96·9 (2)	S–N–Zn	119·7 (2)
C(1)–N–Zn	129·3 (2)	C(1)–N–S	110·8 (2)
N–C(1)–O(1)	123·7 (3)	C(2)–C(1)–O(1)	123·1 (3)
C(2)–C(1)–N	113·2 (3)	C(3)–C(2)–C(1)	129·4 (3)
C(7)–C(2)–C(1)	111·2 (3)	C(7)–C(2)–C(3)	119·4 (3)
C(4)–C(3)–C(2)	118·0 (3)	C(5)–C(4)–C(3)	121·4 (3)
C(6)–C(5)–C(4)	121·0 (3)	C(7)–C(6)–C(5)	116·6 (3)
C(2)–C(7)–S	107·7 (2)	C(6)–C(7)–S	128·7 (3)
C(6)–C(7)–C(2)	123·6 (3)		
(*b*) CDSAC			
O(4)–Cd	2·279 (4)	O(5)–Cd	2·342 (4)
N–Cd	2·323 (4)	O(2)–S	1·441 (3)
O(3)–S	1·435 (3)	N–S	1·632 (4)
C(7)–S	1·755 (4)	C(1)–O(1)	1·240 (3)
C(1)–N	1·357 (4)	C(2)–C(1)	1·504 (5)
C(3)–C(2)	1·382 (4)	C(7)–C(2)	1·386 (4)
C(4)–C(3)	1·390 (4)	C(5)–C(4)	1·391 (4)
C(6)–C(5)	1·386 (4)	C(7)–C(6)	1·376 (4)
O(5)–Cd–O(4)	90·5 (2)	N–Cd–O(4)	93·5 (2)
N–Cd–O(5)	86·7 (2)	O(3)–S–O(2)	116·1 (2)
N–S–O(2)	109·8 (2)	N–S–O(3)	110·6 (2)
C(7)–S–O(2)	110·6 (2)	C(7)–S–O(3)	111·5 (2)
C(7)–S–N	96·6 (2)	S–N–Cd	119·2 (2)
C(1)–N–Cd	129·0 (2)	C(1)–N–S	111·6 (2)
N–C(1)–O(1)	124·2 (3)	C(2)–C(1)–O(1)	122·9 (3)
C(2)–C(1)–N	112·8 (3)	C(3)–C(2)–C(1)	129·5 (3)
C(7)–C(2)–C(1)	111·1 (3)	C(7)–C(2)–C(3)	119·3 (3)
C(4)–C(3)–C(2)	118·3 (3)	C(5)–C(4)–C(3)	121·2 (3)
C(6)–C(5)–C(4)	120·9 (3)	C(7)–C(6)–C(5)	116·7 (3)
C(2)–C(7)–S	107·7 (2)	C(6)–C(7)–S	128·8 (3)
C(6)–C(7)–C(2)	123·5 (3)		

With the results from the present study, full structural data are now available for all members of the series $[M(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$, with $M = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}. The crystal and molecular structures of all the compounds are similar, although the hydrogen bonding involving the H_2O molecules is somewhat different in the Cu complex (Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983).

The M—N and M—O bond distances for all seven complexes are plotted in Fig. 2 along with values of the M^{2+} ionic radii. The basic trends in the M—N, M—O(4) and M—O(5) distances along the series are consistent with the trend in the ionic radii from Mn^{II} to Cd^{II} (Huheey, 1978), with the exception of the Cu complex which shows significant deviation because of the large Jahn–Teller elongation along the Cu—O(5) axis. There also exists, for this complex, a concomitant relative reduction of the Cu—N and Cu—O(4) bonds in the residual square plane.

The M—N bonds are consistently longer than the M—O bonds. Although this would be expected on the basis of the relative atomic radii, the difference, even compared with the longer M—O(5) bonds, is greater than expected. Hence, one may presume that the M—N bond is not very strong. This is not too surprising if we consider that the negative charge on the ligand can be extensively delocalized away from the nitrogen, particularly onto the very electronegative carbonyl and sulphonyl oxygens.

The second feature is that the two unique M—OH_2 bond lengths also differ with the coordinated H_2O

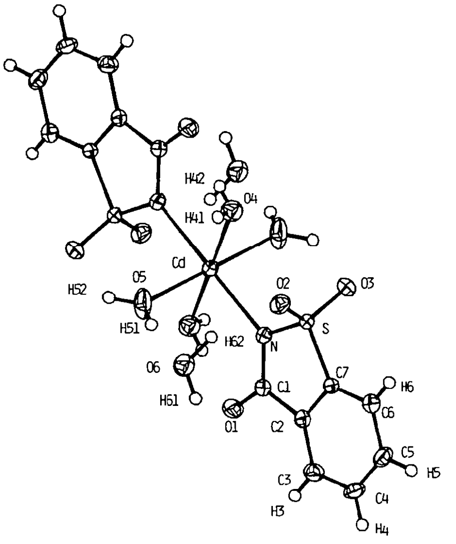

Fig. 1. Molecular structure of $[Cd(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$ with atom numbering in the asymmetric unit.

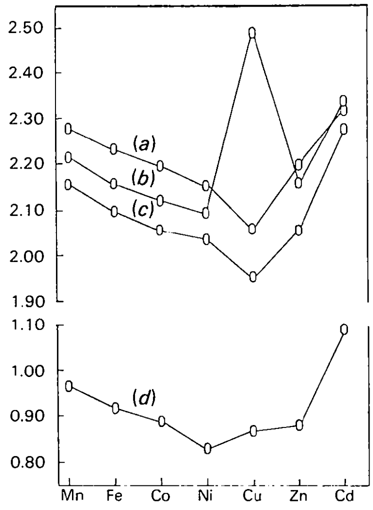

Fig. 2. Trends in the (*a*) M—N, (*b*) M—O(5) and (*c*) M—O(4) bond lengths (Å) in $[M(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$, and (*d*) M^{2+} radii (Å) for CN 6.

molecule [O(4)] giving the shortest *M*—O distance involved in the shortest, and presumably strongest, intermolecular H-bonding. The orientation of the two $C_7H_4NO_3S$ ligands, which are basically coplanar, is such that the ligand planes are close to the plane containing the two nitrogens, the metal and the O(4) oxygens. The dihedral angle between the two planes defined by the ligand ring atoms and the *M*, N and O(4) atoms is ~16°, and that between the ligand plane and the *M*,N,O(5) plane is ~72°. Such an arrangement will place the lone pairs on the sp^2 N atoms approximately parallel to the *M*—O(5) bonds, and it is possible that these will exert some repulsive effect on the O(5) water molecules leading to a weakening of these bonds. It is the *M*—O(5) bond that suffers Jahn–Teller elongation in the Cu complex, and in such distortions it is invariably the weakest bonds that are lengthened. The results of thermal studies of the seven hexahydrates (Haider, Malik & Wadsten, 1983) indicate that the energy of dehydration is minimum for the Cu complex and maximum for the Ni complex. All six H_2O molecules are removed within 350–490 K. The energy of dehydration, which is related to the binding energy of the H_2O molecules in the crystal, increases in the order $Cu < Cd < Mn \sim Zn < Fe \sim Co < Ni$, and has values of 355·8, 385·1, 418·6, 427·0, 594·4, 602·8 and 670·0 Jg^{-1}, respectively.

The saccharinato ligands are planar and have comparable dimensions in all the complexes.

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Dimeric *N-tert*-Butyl(chloroarsine)imine, $C_8H_{18}As_2Cl_2N_2$*

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Abstract. $M_r = 362{\cdot}99$, *Pbca*, $a = 11{\cdot}490\,(2)$, $b = 16{\cdot}093\,(3)$, $c = 15{\cdot}954\,(2)$ Å, $U = 2950{\cdot}0$ Å^3, $Z = 8$, $D_x = 1{\cdot}634$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}86$ mm^{-1}, $F(000) = 1440$, $T = 291$ K, $R = 0{\cdot}036$ for 1410 observed reflections. The As—Cl bonds lie on the same side of the four-membered $[AsN]_2$ ring, and the coordination about N is approximately planar. The two *tert*-butyl groups adopt different conformations, so that the approximate overall molecular symmetry is only *m*. NMR indicates that only one isomer is present in solution.

Introduction. Olah & Oswald (1960) prepared alkyl (chloroarsine)imines $[RNAsCl]_n$ from primary amines and arsenic trichloride; molecular weight measurements indicated $n = 2$ for $R =$ *tert*-butyl, and $n \geq 3$ for other alkyl substituents. Vetter, Strametz & Nöth (1963) also prepared the *tert*-butyl derivative and proposed a dimeric structure. The crystal structure of the methyl analogue (Weiss & Eisenhuth, 1967) showed it to be trimeric with a six-membered $[AsN]_3$ ring. We report here the structure of $[t\text{-BuNAsCl}]_2$, prepared by a new route.

Experimental. 4·6 g $LiN(SiMe_3)(t\text{-Bu})$ in 40 ml *n*-hexane was added slowly to 5·6 g $AsCl_3$ in 50 ml

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* 1,3-Di-*tert*-butyl-2,4-dichlorocyclodiarsazane.

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