

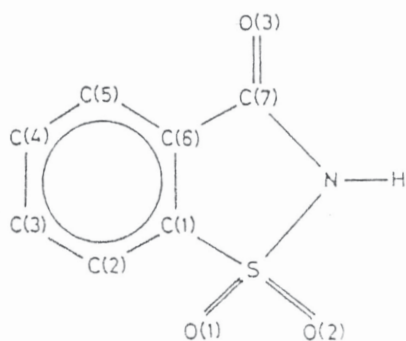
C 12

STRUCTURAL STUDY OF SOME METAL SACCHARINATES

G. Jovanovski & B. Kamenar

Institute of Chemistry, Cyril and Methodius University, Skopje and Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zagreb, Yugoslavia.

Introduction. One of the cyclic imides, commonly used as a sweetening agent, is *o*-sulphobenzimide known as saccharin (see Figure). The chemical properties and especially physiological and biochemical activities of saccharin have been intensively investigated because of its cancerous nature. Defournel [1] was first who reported the possibility of formation of saccharin metal complexes and Font-Altaba [2] was first who published his attempt to solve the structure of Mn saccharinate. Since, on the one hand, many transition elements are very



important in life processes and, on the other hand, very little was known about the crystal structure of metal saccharinates, we started to study the metal complexes of saccharin and solved the structures of $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{sac})_2 \cdot 7\text{H}_2\text{O}$ [3], $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ [4], $\text{Cd}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ [5], $\text{Hg}(\text{sac})_2$ [6], $\text{ClHg}(\text{sac})$ [7], $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ [8] and $\text{Co}(\text{sac})_2 \cdot 2\text{bipy} \cdot \text{H}_2\text{O}$ [9] (sac denoting saccharinate).

Structural study. The X-ray crystal structure analysis revealed that different types of metal-to-ligand bonding exist in the series of different metal saccharinates. Namely, judging from the arrangement of the saccharinate ligands around the central metal atom and comparing the experimentally found interatomic distances between the metal atom and the electron-donor saccharinate atoms (N, O_{SO_2} , O_{CO}), it was concluded that the structures of $\text{Hg}(\text{sac})_2$ and $\text{ClHg}(\text{sac})$ are covalent, those of $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{sac})_2 \cdot 7\text{H}_2\text{O}$ and $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ are ionic, while the structures of $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{sac})_2$.

.2bipy.H₂O are intermediate between the covalent and ionic.

Hg - saccharinates. The structures of Hg(sac)₂ and ClHg(sac) are built up of individual molecules. The mercury atom in both structures has digonal characteristic coordination being bonded to two saccharinate N atoms in the first and to one saccharinate N atom and one Cl atom in the second structure. The Hg-N bond lengths range from 2.02 to 2.06 Å. The mercury atoms in both structures are effectively five-coordinated [10].

Na, Mg and Pb - saccharinates. The structures of Na₃(sac)₃.2H₂O, Mg(sac)₂.7H₂O and Pb(sac)₂.H₂O consist of cations (Na⁺, Mg²⁺ and Pb²⁺, respectively), saccharinate anions and water molecules. All three crystallographically independent Na⁺ ions have C.N. six, being surrounded by O atoms from H₂O molecules, CO and SO₂ groups and saccharinate N atom. Coordination polyhedra are irregular with the Na-O distances from 2.304 to 2.796 Å and Na-N distance of 2.731 Å. The Mg²⁺ ions in the structure of Mg(sac)₂.7H₂O are octahedrally surrounded by five oxygens from H₂O molecules and one O from CO group. Mg-O distances range from 2.012 to 2.113 Å. The Pb²⁺ ion in the structure of Pb(sac)₂.H₂O is surrounded by one O atom from the H₂O molecule, five O atoms from the CO and SO₂ groups and two saccharinate N atoms. The Pb-O and Pb-N distances within the irregular coordination polyhedra vary from 2.435 to 2.901 Å and 2.575 to 2.713 Å, respectively. One of the CO oxygen atoms from two crystallographically independent saccharinate ions is coordinated to two Pb²⁺ ions forming an centrosymmetric Pb²⁺-O-Pb²⁺ bridge with Pb-O distances: 2.697 (2x) and 2.882 Å (2x).

Mn, Cd and Co - saccharinates. Mn atom in Mn(sac)₂.6H₂O and Cd atom in isomorphous Cd(sac)₂.6H₂O, located in the symmetry centres, are octahedrally coordinated by four O atoms from H₂O molecules and two saccharinate N atoms. The Mn-O bond lengths are 2.162 (2x) and 2.219 Å (2x), while the Mn-N bond length is 2.281 Å (2x). The Cd-O and Cd-N distances are 2.285 (2x), 2.354 (2x) and 2.347 Å (2x), respectively. These two compounds are isomorphous with the analogous Fe, Co, Ni and Zn saccharinates. The structure of Co(sac)₂.2bipy.H₂O consists of six-coordinated Co²⁺ ions, saccharinate anions and bipyridyl ligands. Cobalt is

Глигор Јовановски

surrounded by five N atoms (belonging to two bipyridyls and one saccharinate) and one O atom from H₂O molecule. The Co-N bond lengths range from 2.140 to 2.154 Å and the Co-O bond length is 2.054 Å.

Water molecules in all crystallohydrates participate in hydrogen bonding with saccharinate O or N atoms. All saccharinate ligands are planar within the experimental errors. The bond lengths and angles in the six-membered ring of the saccharinate ligands are very similar in all metal saccharinates but which is not the case in the five-membered ring. It seems (see Table) that the C-N-S and O-S-O angles are smaller and N-C-C and N-S-C angles larger in the ionic compounds than those in the covalent ones (including saccharin itself). As far as the interatomic distances are concerned, the C-N and S-N bonds are shorter in the ionic saccharinates than those in the covalent structures. These differences are most probably the consequence of the partial electron density redistribution in the five-membered ring of saccharinate ligand, particularly in its C-N-S fragment.

COMPOUND	ANGLES/°				DISTANCES/Å			
	C-N-S	N-C-C	N-S-C	O-S-O	C-O	S-O	S-N	C-N
SACCHARIN	115.1	109.6	92.2	117.7	1.21	1.42	1.60	1.37
Hg(SAC) ₂	112.8	110.8	95.0	116.1	1.21	1.42	1.65	1.34
ClHg(SAC)	111.2	112.0	96.2	117.2	1.22	1.43	1.67	1.41
Mn(SAC) ₂ ·6H ₂ O	110.9	113.2	96.9	116.1	1.24	1.44	1.63	1.36
Cd(SAC) ₂ ·6H ₂ O	112.8	111.7	95.8	115.6	1.25	1.44	1.62	1.37
Co(SAC) ₂ ·2BIPY·H ₂ O	112.1	111.4	95.7	116.0	1.21	1.44	1.62	1.38
Pb(SAC) ₂ ·H ₂ O	111.1	114.0	95.9	115.2	1.26	1.43	1.60	1.34
Hg(SAC) ₂ ·7H ₂ O	110.7	114.0	97.5	114.6	1.24	1.45	1.62	1.35
Na ₃ (SAC) ₃ ·2H ₂ O	111.2	113.4	97.7	113.6	1.24	1.45	1.60	1.35

References

- ¹Defournel, M. H. Bull. Soc. Chim. 25, 322 (1901)
- ²Font-Altaba, M. Publs. Dept. Cryst. Mineral., Univ. Barcelona, 2, 163 (1956)
- ³Jovanovski, G. & Kamenar, B. Cryst. Struct. Comm. 11, 247 (1982)
- ⁴Kamenar, B. & Jovanovski, G. Cryst. Struct. Comm. 11, 257 (1982)
- ⁵Jovanovski, G. & Kamenar, B. to be published
- ⁶Kamenar, B., Jovanovski, G. & Grdenić, D. Cryst. Struct. Comm. 11, 263 (1982)
- ⁷Ferguson, G., Jovanovski, G., Kaitner, B. & Kamenar, B., to be published
- ⁸Hergold-Brundić, A., Jovanovski, G. & Kamenar, B., to be published
- ⁹Jovanovski, G., Kamenar, B. & Nagl, A. God. Jugosl. cent. kristalogr. 18, 69 (1983)
- ¹⁰Grdenić, D. Quart. Rev., 19, 303 (1965)