Quim. Nova, Vol. 28, No. 2, 326-328, 2005

THE SACCHARINATE ANION: A VERSATILE AND FASCINATING LIGAND IN COORDINATION CHEMISTRY[#]

Enrique J. Baran
Centro de Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.Correo 962, 1900 La Plata, Argentina

Recebido em 14/6/04; publicado na web em 12/11/04

The saccharinate anion, obtained by deprotonation of the N-H moiety of saccharin (o-sulfobenzimide) is a very versatile and polyfunctional ligand in coordination chemistry. In this review the different forms of metal-to-ligand interactions involving this anion and some other coordination peculiarities are briefly discussed on the basis of some selected examples.

Keywords: saccharin; saccharinate; metal complexes; metal-saccharinate bonds.

INTRODUCTION

Saccharin (o-sulfobenzimide; 1,2-benzothiazole-3(2H)-one 1,1 dioxide; Hsac, Figure 1) is one of the best known and most widely used artificial sweetening agents. Initially, investigation of the interaction of saccharin with different biologically relevant cations attracted great interest due to the suspected carcinogenicity of this compound[1-3] which, notwithstanding, was recently definitively ruled out[3,4]. However, simultaneously these studies show that its coordination chemistry is very interesting and versatile as the saccharinate anion, obtained by deprotonation of the NH group, offers different coordination sites to metallic centers, i.e. one **N**, one **O** (carbonylic) and two **O** (sulfonic) atoms.

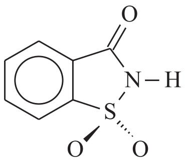

Figure 1. *Schematic structure of saccharin (Hsac)*

Most of the initially prepared complexes were mixed aquo-saccharinate species, but a great number of other mixed ligand complexes, with a variety of organic ligands have also been prepared and characterized in the last years. In most of these species the metal-saccharinate interaction takes place in different ways documenting its potentiality as a polyfunctional ligand in coordination chemistry.

In this brief overview we would like to give an insight into the fascinating chemistry derived from this simple molecule, on the basis of some selected examples.

Ionic saccharinates

There is a number of saccharinate derivatives, containing alkaline or alkaline-earth cations in which the cation/anion interaction is mainly of ionic nature. This is the case of $Na(sac).2/3H_2O$ and $Mg(sac)_2.7H_2O$[5] of $K_2Na(sac)_3.H_2O$[6] and also of $NH_4(sac)$[7].

Monodentate N-coordinated metal complexes

All the divalent cations of the first transition metal series (V-Zn) show a clear preference to interact with the saccharinate anion through its deprotonated **N** atom, generating tetraaquabis(saccharinate) complexes, $[M^{II}(sac)_2(H_2O)_4]$, with the saccharinate ligands in *trans* position[8-10].

Besides, a great number of mixed ligand complexes of these same metals interact also with saccharinate in the same way. Some examples of compounds of this type are: the tetrahedral complexes $[Zn(sac)_2(py)_2]$ (py = pyridine)[11] and $[Zn(sac)_2(im)_2]$ (im = imidazole)[12], the square-pyramidal species $[Cu(H_2O)(sac)_2(py)_2]$[13], $[Cu(H_2O)(sac)_2(bzim)_2]$ (bzim = benzimidazole)[14] , and $[Cu(H_2O)(sac)_2(nic)_2]$ (nic = nicotinamide)[15] and the octahedral complex $[Ni(sac)_2(ea)_2]$ (ea = monoethanolamine)[16].

Also in some Pd(II) and Pt(II) complexes of the type $[MCl(sac)L_2]$ (L = different phosphine ligands) coordination of saccharinate also involves Pd-N and Pt-N bonds[17].

Finally, one must mention that some heavy non-transition metal cations interact with the saccharinate anion in the same way as shown, for example, by the following species: $[Hg(sac)_2(bipy)]$ (bipy = 2,2'-bipyridyl)[18], $[Hg(sac)_2(ea)_2]$[19], $[Cd(sac)_2(pyet)_2]$ (pyet = 2-pyridylethanol)[20], $[Cd(sac)_2(diet))_2]$ (diet = diethanolamine)[21], and $[Cd(sac)_2(NH_3)_4]$[22].

Monodentate O-coordinated metal complexes

The carbonyl O-atom often participates in bonding, when saccharinate acts as a bidentate ligand, as shall be discussed below, but monodentate coordination by this O-atom is rather unusual. The first example of this form of interaction was reported for a V(II) complex, namely $[V(sac)_2(py)_4].2py$[23]. Similar M-O bonds were found latter in the cases of $[Ni(sac)_2(py)_4]$[24] and bis(saccharinate) tetra(isoquinoline)copper(II)[25]. Taking into account that, as mentioned above, the lighter divalent transition metal cations prefer M-N interactions, the appearance of M-O bonds in the mentioned complexes may probably be originated by steric effects. This last supposition is additionally confirmed by the structure of the copper (I) complex of composition $[Cu(sac)(PPh_3)_3]$, containing the bulky triphenilphosphine ligands (PPh_3), in which saccharinate also coordinates through the carbonyl O-atom[26] whereas, interestingly, in a similar compound with one PPh_3 group less, $[Cu(sac)(PPh_3)_2]$, the coordination occurs through the N-atom[26].

---

*e-mail: baran@quimica.unlp.edu.ar

[#] Conferência proferida na 27ª RASBQ, em Salvador - BA, 2004

Bidentate N,O- coordinated metal complexes

In this case the saccharinate moiety can act either as a single bidentate ligand for only one metal center or, more frequently, as a bidentate bridging ligand. A recent example for the first situation is the complex $[Pb(sac)_2ophen(H_2O)_2]$ (ophen = 1,10-phenanthroline) in which Pb(II) presents the unusual coordination number eight, with the two saccharinate anions acting as bidentate and the coordination sphere completed by the two N atoms of ophen and the two water O-atoms[27]. In the case of the simpler $[Pb(sac)_2].H_2O$ complex, the bidentate ligand originates a dimeric structure[28].

A dimeric structure also exists in the case of $[Cd(sac)_2(im)_2]_2$ in which two of the four saccharinate moieties act as bridging ligands whereas the other two coordinated through the N-atom, one to each Cd(II) center[29]. A copper(II) complex of the same stoichiometry and with similar bond characteristics are also known[30].

Also in the case of the above mentioned Cu(I)/triphenyphosphine complexes a dinuclear species of composition $[Cu(sac)(PPh_3)]_2$ could be prepared, in which the metal centers are bridged by the two bidentate saccharinate anions[26].

Nevertheless, probably the most interesting dimeric species of this type is the $[Cr_2(sac)_4py_2].2py$ complex[31], in which the four saccharinate moieties act as bidentate bridges between the two Cr(II) cations and which therefore resembles the well known Cr(II)/carboxylate species[32].

Complex polymeric species

In some cases the bridging ability of saccharinate generates more complex structures. One specially interesting example in this context is the recently reported polymeric Tl(I) complex of composition $[Tl_2(sac)_2(H_2O)]_n$. Its structure shows two structurally different metallic centers, one of them presents coordination 8 and the other one coordination 5. The saccharinate anion shows an unprecedented coordination behavior as it acts as chelating ligand through its N and carbonyl O atoms with the N atoms interacting simultaneously with both metal centers and also the sulfonyl O-atoms are involved in bonding[33].

Moreover, silver saccharinate presents an infinite chain structure conformed by dimeric units in which each Ag(I) cation is coordinated to a N atom of one saccharinate anion and to one carbonylic oxygen atom from another one. The dimeric units are combined to infinite chains by additional participation of sulfonyl O-atoms[34].

Therefore, these two complexes constitute examples of saccharinate moieties acting as tridentate ligands.

Saccharinate complexes of the trivalent lanthanides

The saccharinate complexes of the trivalent lanthanides and yttrium, constitute an especially interesting series of compounds. They belong to three different structural types. In the first family, of composition $[Ln(sac)(H_2O)_8](sac)_2.H_2O$, with Ln = La, Ce, Pr, Nd, Sm, Eu, the Ln(III) cation is in a tricapped trigonal prismatic environment with nine-fold oxygen coordination, involving one saccharinate carbonylic O-atom and eight water O-atoms [35,36]. The second group of composition $[Ln(sac)_2(H_2O)_6](sac)(Hsac).4H_2O$ with Ln = Gd, Dy, Ho, Er, Yb, Lu, Y constitutes an interesting example of complexes that contain simultaneously saccharin and its anion in the crystal lattice [36]. In the third group, the Tm(III) and Tb(III) compounds, present two closely related structures conformed by three and two $[Ln(sac)(H_2O)_7]^{2+}$ crystallographically independent complexes, respectively, with the $[Tm(sac)(H_2O)_7]_3(sac)_6.9H_2O$ and $[Tb(sac)(H_2O)_7]_2(sac)_3.6H_2O$ composition. For all the heavier lanthanides (Gd-Lu) and yttrium the cation presents eight-fold oxygen coordination, with the ligands arranged at the corners of a slightly distorted square Archimedean antiprism[36]. Interestingly, the Tm(III) compound presents one of the biggest so far reported unit cell volumes ($V = 4826.6$ Å^3)[36] for any inorganic complex.

Other peculiar coordination behavior

Some saccharinate complexes present a very particular coordination characteristic, which exemplify another fascinating aspect of this ligand. This peculiarity, that was first found in two copper(II) complexes, namely $[Cu(sac)_2(py)_3]$[37] and $[Cu(sac)_2(dipyr)(H_2O)]$ (dipyr = dipyridylamine)[38,39], is the fact that the they are simple mononuclear complexes in which one of the saccharinate ligands is bonded through the N-atom and the other one through the O-atom. A similar behavior was also observed with some mixed ligand complexes containing 2-pyridylmethanol (mpy), i.e., $[Cd(sac)_2(mpy)_2]$[40], $[Zn(sac)_2(mpy)_2]$[40] , $[Co(sac)_2(mpy)_2]$[41], $[Ni(sac)_2(mpy)_2]$[41].

Presence of bonded and not bonded saccharinate anions and of free saccharin in complex species

Another interesting aspect, recently documented in a variety of compounds, is the fact that in some species the saccharinate anion can be present both in the complex cation and as a counter-ion, outside the coordination sphere. Some examples have been presented above, in relation to the stoichiometries of the complexes of the heavier lanthanides[36]. Other examples are found in the complexes $[Cu(sac)(bipy)_2](sac).2H_2O$[42], $[Mn(sac)(bipy)_2(H_2O)](sac)$[43], $[Co(sac)(bipy)_2(H_2O)](sac)$[44], and $[Mn(sac)(ophen)_2(H_2O)](sac)$[44].

Obviously, an important number of compounds in which the saccharinate anion is only present as a counter anion from a complex cation are also known. Some recently reported examples are the following: $[Cu_2(\mu\text{-oxal})(bipy)_2(H_2O)_2](sac)_2$ with oxal = oxalate[45], $[Cd(tea)_2](sac)_2$ and $[Hg(tea)_2](sac)_2$ with tea = triethanolamine[46], $[Co(H_2O)_4(py)_2](sac)_2$[47], $[Ni(H_2O)_4(py)_2](sac)_2$[47], $[Co(dmpy)_2](sac)_2$ and $[Co(dmpy)_2](sac)_2$ with dmpy = pyridine-2,6-dimethanol[48], $[Fe(4,4'\text{-bipy})(H_2O)_4](sac)_2$ with 4,4'-bipy = 4,4'-bipyridine[49], $[M(nic)_2(H_2O)_4](sac)_2$ with M = Co(II), Ni(II), Zn(II)[50]. An especially interesting example of systems of this type is the material of composition $[Cu(4,4'\text{-bipy})_2(H_2O)_2](sac)_2.DMF$ which is a square grid polymer with the saccharinate anions sandwiched between the complex layers and the dimethylformamide (DMF) molecules filling the square holes[51].

Besides, the presence of free saccharin in the crystal lattices of certain complexes have been established, as mentioned above in the case of the $[Ln(sac)_2(H_2O)_6](sac)(Hsac).4H_2O$ complexes[36]. Notwithstanding, the first case in which this situation was found is, apparently, the VO^{2+} complex of composition $[VO(OH)(sac)\ (H_2O)_2(Hsac)]$[52].

Another example recently discussed by two independent research groups is the case of $[Fe(ophen)_3](sac)_2.Hsac.6H_2O$[53,54]. On the other hand, this behavior was also recently described in one alkaline salt, i.e., $Cs(sac)Hsac.H_2O$[55].

CONCLUDING REMARKS

In this overview we have attempted to give a brief insight into the peculiarities and versatility of the saccharinate anion as a ligand in coordination chemistry. As this anion acts as a polyfunctional ligand it is capable not only to interact with metal centers in different ways, but also to generate relatively strong interactions in the crystalline environments that it builds up, mostly through hydrogen bonding.

The so far accumulated X-ray structural data of a great number of saccharinate complexes allowed to confirm different forms of ligand-to-metal interactions that involve: a) monodentate M-N or M-O(carbonyl) bonds; b) bidentate N-M-O bonds; c) bridging M-N-C=O-M bonds; d) M-N, M-O(carbonyl) and M-O(sulfonyl) bonds that generate polymeric structures, e) M-O and M-N bonds from two different saccharinate anions in the same complex moiety; f) purely ionic interactions between a cation and the saccharinate anion.

Studies of mixed ligand complexes containing saccharinate and some other ligands have demonstrated that the coordination mode of saccharinate is highly adaptable to the steric requirements of the complex formed.

The coexistence of bonded and non-bonded saccharinate anions has also been demonstrated in a number of cases. Also the presence of non-deprotonated saccharin molecules in a number of complex structures has been established.

On the other hand, the important and continuous synthetic work developed in recent years with metal saccharinates has shown that most of them may be useful starting materials for the preparation of other complexes and also for the development of interesting new materials.

ACKNOWLEDGMENTS

It is a great pleasure to acknowledge the contributions of colleagues and collaborators whose names appear in the references. Work from our laboratory reported here was supported by the *Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina* (CONICET) and the *Agencia Nacional de Promoción Científica y Tecnológica*. The author is a member of the Research Career from CONICET.

ABBREVIATIONS

bipy = 2,2'-bipyridyl
4,4'-bipy = 4,4'-bipyridine
bzim = benzimidazole
diet = diethanolamine
dipyr = dipyridylamine
dmpy = pyridine-2,6-dimethanol
ea = monoethanolamine
Hsac = saccharin
im = imidazole
mpy = 2-pyridylmethanol
nic = nicotinamide
ophen = 1,10-phenanthroline
oxal = oxalate
PPh_3 = triphenlylphosphine
py = pyridine
pyet = 2-pyridylethanol
sac = saccharinate
tea = triethanolamine

REFERENCES

1. Suzuki, N.; Suzuki, H.; *Cancer Res.* **1995**, *55*, 4253.
2. Zurlo, J.; Squire, R.A.; *J. Natl. Cancer Inst*. **1998**, *90*, 2.
3. Weihrauch, M.R.; Diehl, V.; Bohlen, H.; *Mediz. Klin.* **2001**, *96*, 670.
4. *Chem. Brit.* **2001**, *37*, 18.
5. Jovanosvski, G.; Kamenar, B.; *Cryst. Struct. Commun*. **1982**, *11*, 247.
6. Malik, K.M.A.; Haider, S. Z.; Hossain, M. A.; Hursthose, M. B.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 1696.
7. Ng, S.W.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 649.
8. Haider, S. Z.; Malik, K. M. A.; Ahmed, K. J.; Hess, H.; Riffel, H.; Hursthouse, M. B.; *Inorg. Chim. Acta* **1983**, *72*, 21.
9. Cotton, F. A.; Lewis, G. E.; Murillo, C. A.; Schwotzer, W.; Valle, G.; *Inorg. Chem.* **1984**, *23*, 4038.
10. Cotton, F. A.; Falvello, L. R.; Murillo, C.A.; Valle, G.; *Z. Anorg. Allg. Chem.* **1986**, *540/541*, 67.
11. Quinzani, O. V.; Tarulli, S.; Piro, O. E.; Baran, E. J.; Castellano, E. E.; *Z. Naturforsch., B: Chem. Sci.* **1997**, *52*, 183.
12. Williams, P. A. M.; Ferrer, E. G.; Correa, M. J.; Baran, E. J.; Castellano, E. E.; Piro, O. E.; *J. Chem. Crystallogr.* **2004**, *34*, 285.
13. Jovanovski, G.; Naumov, P.; Grupce, O.; Kaitner, B.; *Eur. J. Solid State Inorg. Chem.* **1998**, *35*, 231.
14. Williams, P. A. M.; Ferrer, E. G.; Pasquevich, K. A.; Baran, E. J.; Chaia, Z.; Castellano, E. E.; Piro, O. E.; *Z. Anorg. Allg. Chem.* **2000**, *626*, 2509.
15. Parajón-Costa, B. S.; Baran, E. J.; Piro, O. E.; Castellano, E. E.; *Z. Naturforsch., B: Chem. Sci.* **2002**, *57*, 43.
16. Andac, O.; Topcu, Y.; Yilmaz, V. T.; Harrison, W. T. A.; *J. Chem. Crystallogr.* **2000**, *30*, 767.
17. Henderson, W.; Nicholson, B. K.; McCaffrey, L. J.; *Inorg. Chim. Acta* **1999**, *285*, 145.
18. Hergold-Brundic, A.; Kamenar, B.; Jovanovski, G.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *45*, 556.
19. Topcu, Y.; Andac, O.; Yilmaz, V. T.; Harrison, W. T. A.; *Cryst. Res. Technol.* **2002**, *37*, 509.
20. Yilmaz, V. T.; Hamamci, S.; Thöne, K.; *Z. Anorg. Allg. Chem.* **2003**, *629*, 711.
21. Andac, O.; Topcu, Y.; Yilmaz, V. T.; Harrison, W. T. A.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *58*, M14.
22. Pascual, I.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 2028.
23. Cotton, F. A.; Falvello, L. R.; Llusar, R.; Libby, E.; Murillo, C. A.; Schwotzer, W.; *Inorg. Chem.* **1986**, *25*, 3423.
24. Quinzani, O. V.; Tarulli, S.; Marcos, C.; García Granda, S.; Baran, E. J.; *Z. Anorg. Allg. Chem.* **1999**, *625*, 1848.
25. Naumov, P.; Jovanovski, G.; Ristova, M.; Abdul Razak, I.; Çakir, S.; Chantrapromma, S.; Fun, H. K.; Ng, S. W.; Z. *Anorg. Allg. Chem.* **2002**, *628*, 2930.
26. Falvello, L. R.; Gomez, J.; Pascual, I.; Tomás, M.: Urriolabeitía, E.; Schultz, A. J.; *Inorg. Chem.* **2001**, *40*, 4455.
27. Baran, E. J.; Wagner, C. C.; Rossi, M.; Caruso, F.; *Z. Anorg. Allg. Chem.* **2000**, *626*, 701.
28. Jovanovski, G.; Hergold-Brundic, A.; Kamenar, B.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *44*, 63.
29. Li, J.; Ke, Y.; Wang, Q.; Wu, X.; *Cryst. Res. Technol.* **1997**, *32*, 481.
30. Liu, S. X.; Huang, J. L.; Li, J. M.; Lin, W. B.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 41.
31. Alfaro, N. M.; Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; *Inorg. Chem.* **1992**, *31*, 2718.
32. Cotton, F. A.; Wilkinson, G.; Murillo, C.; Bochmann, M.; *Advanced Inorganic Chemistry*, 6th 3ed., J. Wiley & Sons, New York, 1999.
33. Baran, E.J.; Wagner, C.C.; Rossi, M.; Caruso, F.; *Z. Anorg. Allg. Chem.* **2001**, *627*, 85.
34. Weber, R.; Gilles, M.: Bergerhoff, G.; *Z. Kristallogr.* **1993**, *206*, 273.
35. Starynowicz, P.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 2063.
36. Piro, O. E.; Castellano, E. E.; Baran, E. J.*; Z. Anorg. Allg. Chem.* **2002**, *628*, 612.
37. Quinzani, O. V.; Tarulli, S. H.; García-Granda, S.; Marcos, C.; Baran, E. J.; *Cryst. Res. Technol.* **2002**, *37*, 1338.
38. Naumov, P.; Jovanovski, G.; Drew, M. G. B.; Ng, S. W.; *Inorg. Chim. Acta* **2001**, *314*, 154.
39. Deng, R. M. K.; Dillon, K. B.; Goeta, A. E.; Mapolelo, M.; *Inorg. Chim. Acta* **2001**, *315*, 245.
40. Yilmaz, V. T.; Guney, S.; Andac, O.; Harrison, W. T. A.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *58*, M427.
41. Yilmaz, V. T.; Guney, S.; Andac, O.; Harrison, W. T. A.; *Polyhedron* **2002**, *21*, 2393.
42. Hergold-Brundic, A.; Grupce, O.; Jovanovski, G.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 2659.
43. Dillon, K. B.; Bilton, C.; Howard, J. A. K.; Hoy, V. J.; Deng, R. M. K.; Sethatho, D. T.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 330.
44. Deng, R. M. K.; Bilton, C.; Dillon, K. B.; Howard, J. A. K.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 142.
45. Li, J.; Sun, J.; Chen, P.; Wu, X.; *Cryst. Res. Technol.* **1995**, *30*, 353.
46. Andac, O.; Topcu, Y.; Yilmaz, V. T.; Guven, K.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2001**, *57*, 1381.
47. Jovanovski, G.; Naumov, P.; Grupce, O.; Kaitner, B.; *Eur. J. Solid State Inorg. Chem.* **1998**, *35*, 579.
48. Andac, O.; Guney, S.; Topcu, Y.; Yilmaz, V. T.; Harrison, W. T. A.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *58*, M17.
49. Williams, P. A. M.; Ferrer, E. G.; Baran, E. J.; Piro, O. E.; Ellena, J.; Castellano, E. E.; *J. Argent. Chem. Soc.* **2002**, *90*, 109.
50. Castellano, E. E.; Piro, O. E.; Parajón-Costa, B. S.; Baran, E. J.*; Z. Naturforsch., B: Chem. Sci.* **2002**, *57*, 657.
51. Williams, P. A. M.; Ferrer, E. G.; Baran, E. J.; Piro, O. E.; Castellano, E. E.; *Z. Anorg. Allg. Chem.* **2002**, *628*, 2044.
52. Ferrer, E. G.; Etcheverry, S. B.; Baran, E. J.; *Monatsh. Chem.* **1993**, *124*, 355.
53. Williams, P. A. M.; Ferrer, E. G.; Pasquevich, K. A.; Baran, E. J.; Castellano, E. E.; Piro, O. E.; *J. Chem. Crystallogr.* **2000**, *30*, 539.
54. Deng, R. M. K., Simon, S.; Dillon, K. B.; Goeta, A. E.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2001**, *57*, 4.
55. Naumov, P.; Jovanovski, G.; *Vib.. Spectrosc.* **2000**, *24*, 201.