

INFRARED STUDY OF THE BINUCLEAR CADMIUM(II) IMIDAZOLE SACCHARINATO COMPLEX: COMPARISON WITH THE COPPER(II) COMPOUND

Panče Naumov and Gligor Jovanovski

*Institute of Chemistry, Faculty of Science, "Sv. Kiril i Metodij" University, PO Box 162,
91001 Skopje, Macedonia; E-mail: spance@iunona.pmf.ukim.edu.mk*

(Received 13.11.1998)

Abstract

FT IR spectra of protiated and iminodeuterated cadmium(II) imidazole saccharinato complex at room (RT) and liquid-nitrogen temperature (LNT) in the 4000-500 cm⁻¹ region were recorded. The bands that are mainly due to the stretching modes of the imino, carbonyl and sulphonyl groups were assigned. The spectra in the NH and ND stretching regions were discussed in sense of the available structural data. On the basis of comparison with the similar copper(II) compound and other metal saccharinates, the spectral appearance in the regions of CO and SO₂ stretchings was used to make certain structural predictions.

INTRODUCTION

Since the compounds of saccharin¹ with various metals were suspected to be potentially carcinogenic, a notable interest has been shown to study their structural properties. The saccharinato salts and complexes are thus, both structurally and spectroscopically, well investigated. Recently, however, the research work in this field has been expanded over the adducts of the saccharinates with various aromatic nitrogen bases. It seems reasonable to expect that such compounds, compared to the corresponding saccharinates, will show altered physiological properties. In this sense, bearing in mind the

¹ The systematic name of saccharin is 1,2-benzisothiazol-3(2H)-one 1,1-dioxide.

presence of imidazole ring in numerous naturally abundant compounds, the adducts of *imidazole* are of a scientific interest. As a part of our extensive study on saccharinates, we recently investigated the spectral properties of several imidazole saccharinato complexes.

Up to now, the structures of Co(II) [1], Ni(II) [2], Cu(II) [3] and Cd(II) [4] imidazole saccharinates were reported. The binuclear copper(II) and cadmium(II) compounds, however, having the general formula $[M_2(HIm)_4(sac)_4]^2$, are rather special. In their structure, namely, both *N*-donating and bidentate bridging saccharinato ligands were found. For the cadmium compound³, however, only limited data, such as the basic structural parameters and some data pertaining to the coordination polyhedron of the metal atom and the hydrogen bonding, were reported [4], while no reference to eventually deposited data was made. Thus, the existing structural data on this complex are rather scarce and incomplete. On the other hand, except for the electronic absorption spectra of the compounds [1, 2, 5] and the FT IR spectra of copper(II) imidazole saccharinate, recently studied by us [6], no detailed infrared study of these complexes exist.

In order to obtain certain structural information about the imidazole adduct of cadmium(II) saccharinate, the RT and LNT FT IR spectra of its protiated as well as of its iminodeuterated analogue with a low deuterium content were recorded. On the basis of the previous spectra-structural inferences in various saccharinates and imidazole complexes and the comparison with the similar copper(II) compound [6], the characteristic bands in the infrared spectrum of the title compound were assigned. The spectra in the NH and ND stretching regions were discussed in connection with the available structural data, while the CO and SO₂ stretching regions were used to make certain structural predictions.

EXPERIMENTAL

The complex was synthesized by an addition of aqueous solution of cadmium(II) acetate to a warm, stirred aqueous solution of saccharin and imidazole in stoichiometric ratio. Colorless prismatic crystals of the compound were obtained at RT. No spectral

² In what follows, the acronyms *HIm*, *py*, *Hsac* and *sac* denote imidazole, pyridine, saccharin and saccharinato ion or a ligand, respectively.

change was observed after recrystallization from aqueous solution. The results from the elemental (C, H, N) analysis corresponded to the given formula [4].

The spectra of the protiated as well as of the deuterated samples were recorded from KBr pellets with a System 2000 FT IR interferometer (Perkin Elmer). The resolution was 2 cm^{-1} ; 64 sample spectra were averaged. For the spectra recorded at LNT a P/N 21525 variable temperature cell (Graseby Specac) equipped with KBr windows was employed. The band fitting was performed with the program GRAMS/386 [7].

Partially deuterated analogue of the complex was obtained by exposing powdered protiated sample to D_2O vapors in an evacuated desiccator overnight. Sufficiently high vacuum was used to prevent the H/D exchange with air. Since that the aim of the deuteration was to shift the imino stretchings to lower frequencies and thus avoid the presence of the C-H stretching modes and/or eventual interactions with other modes expected in the same region, no deuteration to higher degree was attempted.

CRYSTALLOGRAPHIC DATA

Cadmium(II) imidazole saccharinate [4], as well as the similar copper(II) compound [3], is monoclinic⁴. Corresponding space groups of the cadmium and copper complex were found to be $C2/c$ and $P2_1/n$, respectively. The basic structural moiety of both complexes is a dimer composed of two $\text{M}(\text{HIm})_2(\text{sac})_2$ units (M denoting Cd or Cu) connected through a symmetry center. Both saccharinato ligands of the monomer unit are *N*-coordinated to the metal atom. One of them, however, is bridging and through its carbonyl oxygen is coordinated to the other metal atom. So, two amidato-like bridging saccharinato ligands and two metal atoms close almost planar octagonal ring. Because of the symmetry center, only two non-equivalent saccharinato ligands as well as two imidazole ligands exist in the structure.

The surrounding of the metal atom is described as a trigonal-bipyramide. It is formed by two saccharinato nitrogen atoms (one of the saccharinato ligands is *N*-donating

³ The systematic name of the complex is: bis[μ -1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido-*kN:kO*]bis[1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido-*kN*]tetrakis(imidazole)dicalcium(II).

⁴ Hereafter often referred to as cadmium and copper complex, respectively.

and the other one is bridging) and a carbonyl oxygen from the bridging saccharinato ligand coordinated to the neighboring metal atom. Two imidazole nitrogen atoms occupy the apical positions.

RESULTS AND DISCUSSION

The infrared spectra of the cadmium complex in 4000-500 cm^{-1} region at RT and LNT are shown in Fig. 1.

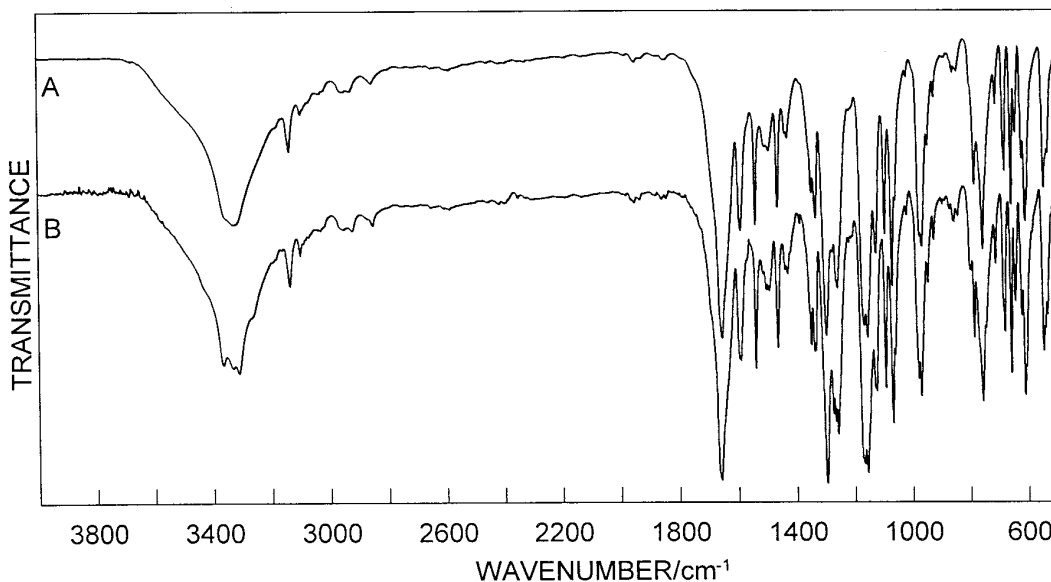


Fig. 1. The RT (A) and LNT (B) FT Infrared Spectra of $[\text{Cd}_2(\text{HIm})_4(\text{sac})_4]$

NH and ND stretching regions

The deprotonation of saccharin on conversion to the corresponding ligand is followed by absence of the $\nu(\text{NH})$ band in the spectra of its complexes. Only one case was so far described where whole saccharin molecule is included in the structure [8]. On the other hand, the series of overlapping bands characterizing the 3300-2100 cm^{-1} region of the solid-state spectrum of imidazole [9, 10], besides the $\nu(\text{CH})$ bands, is usually replaced by one or possibly two fairly strong and sharp NH stretching bands in the 3500-3100 cm^{-1}

region upon complexation [10, 11]. Similar spectral appearance is observed in the spectrum of the studied complex (Fig. 1).

The comparison of the NH stretching region in the RT infrared spectra of the cadmium and the copper complex is shown in Fig. 2A. In the spectrum of the cadmium complex a strong asymmetric band with a maximum at 3325 cm^{-1} (accompanied with

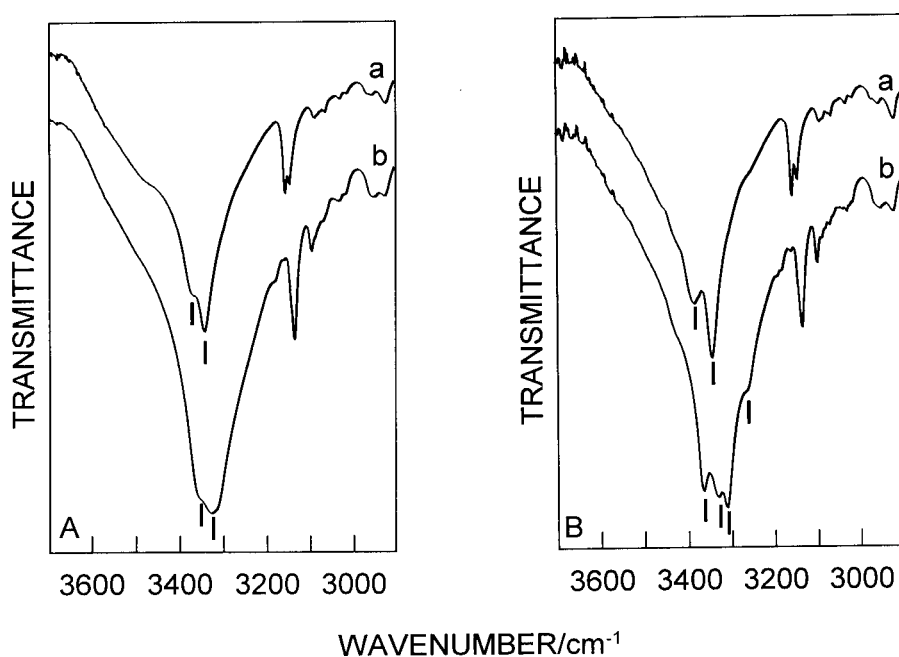


Fig. 2. The NH Stretching Region in the RT (A) and LNT (B) Spectra of $[\text{Cu}_2(\text{HIm})_4(\text{sac})_4]$ (a) and $[\text{Cd}_2(\text{HIm})_4(\text{sac})_4]$ (b)

a shoulder around 3352 cm^{-1}) is present. Similarly, an asymmetric band with a shoulder on its high-frequency side can be seen in the spectrum of the copper complex. On lowering the temperature, the shoulder (3352 cm^{-1}) in the spectrum of the Cd complex shifts to higher frequencies and appears as a separate band at 3363 cm^{-1} at LNT (Fig. 2B). Additionally, the RT band at 3325 cm^{-1} undergoes splitting into two bands with maxima at 3328 and 3309 cm^{-1} . Thus the complex RT band in the $\nu(\text{NH})$ region consists of most probably *three* subbands, accompanied with a shoulder around 3262 cm^{-1} . Likewise, in the LNT spectrum of the copper complex the shoulder (3370 cm^{-1} , RT) also separates in a band (3383 cm^{-1}) at LNT, but the band present at RT (3343 cm^{-1}) practically does not change

its position (Fig. 2B). So, in fact, only *two* overlapped and fairly strong bands are present in the region of the spectrum of the Cu complex where the $\nu(\text{NH})$ modes are expected.

The above mentioned shoulder in the RT spectrum of the studied compound appeared on the higher-frequency side of the strongest band in this region (3352 cm^{-1}), shifts considerably to higher frequencies on lowering the temperature (11 cm^{-1}) giving a separate band at LNT (Fig. 2B). Similarly to the copper complex [6], it can be supposed that this band is related to an imino group involved in highly bent hydrogen bonding [12]. However, since the precise structural data for the studied complex are not available, this can not be certified as in the case of the copper complex.

The $\nu(\text{NH})$ bands in the spectrum of the Cd complex are generally found at *lower* frequencies than in the case of the Cu complex (Fig. 2). The spectral data are thus in accordance with the structural ones revealing shorter $\text{N}\cdots\text{O}$ distances in the former [$2.849(7)$ and $2.905(7)\text{ \AA}$] [4] compared to the latter compound (2.911 , 2.947 , 2.953 and 3.021 \AA ⁵) [3]. If only this fact is taken into consideration, then somewhat *stronger* $\text{NH}\cdots\text{O}$ hydrogen bonds could be supposed to exist in the case of the Cd complex. In such considerations, however, one should not exclude the previously mentioned possibility of pronounced asymmetry within the NHO system.

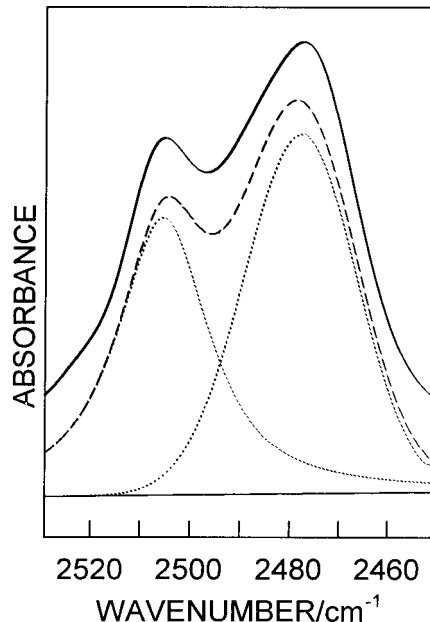
As it was already mentioned, the structure determination [4] revealed two intermolecular hydrogen bonds between the imidazole imino groups and sulphonyl oxygen atoms in Cd imidazole saccharinate. According to the above discussion, it is to expect that the non-equivalent imino groups participate in hydrogen bonding of different strength. The appearance of *three* $\nu(\text{NH})$ bands at LNT in the case of the studied compound, however, does not correspond to the existence of *two* non-equivalent imino groups in the structure. Contrary, an equivalence between the number of crystallographically different NH groups and the number of $\nu(\text{NH})$ bands was found for the copper complex [6]. Having in mind the lower $\nu(\text{NH})$ frequencies for the cadmium complex compared to the copper complex, one may expect the appearance of three bands to be due to eventual vibrational interaction between the $\nu(\text{NH})$ modes and non-fundamental vibrational modes expected in the same region.

⁵ The corresponding e.s.d.'s are not given in the Ref. 3.

In order to inspect this presumption and thus enhance the assignment, the spectrum of slightly deuterated analogue of the studied complex was recorded. The iminodeuteration, namely, was expected to shift the imino stretching bands and thus avoid the interaction with the eventual second-order vibrational modes expected in the $\nu(\text{NH})$ region. As noticed earlier, the imidazole imino groups undergo H/D exchange [13], although the complete and selective deuteration of imidazole is known to be troublesome.

The $\nu(\text{ND})$ region in the difference LNT spectrum⁶ of the slightly deuterated sample (deuteration of less than 5 %) is shown in Fig. 3A. Evidently, only *two* bands (at 2506 and 2476 cm^{-1}) appear. Two bands, with maxima at 2505 and 2478 cm^{-1} could be also resolved by curve-fitting (Fig. 3). The appearance of two $\nu(\text{ND})$ bands is in accordance with the existence of two crystallographically different NH groups in the structure [4]. The band at 2476 cm^{-1} would correspond to the shorter N...O distance [2.849(7) Å] and the less intense band at 2506 cm^{-1} could be prescribed to the longer N...O distance

Fig. 3. The Original (Full Line) and Reconstructed (Dashed Line) LNT Difference Spectrum of



[Cd₂(HIm)₄(sac)₄] in the $\nu(\text{ND})$ Region (The Component Bands are Shown with Dotted Lines)

⁶ The difference spectrum was obtained by subtracting the scaled LNT spectrum of the protiated sample from the LNT spectrum of the deuterated one.

[2.905(7) Å]. As expected, the $\nu(\text{ND})$ bands for the studied complex are found at lower frequencies than the corresponding bands in the case of the Cu complex (2522 and 2493 cm^{-1}) [6]. The intensity difference of the two $\nu(\text{ND})$ bands, however, remains unclear.

Carbonyl stretching region

The assignment of the carbonyl stretching bands in the spectra of the saccharinato compounds is known to be followed by difficulties [14-16]. Namely, additional bands, such as those arising from some benzenoid stretching modes of the saccharinato ligand, are expected in the same region. It is known, however, that the benzenoid stretching modes can be distinct from the carbonyl stretching bands by being sharper and somewhat less intense and usually appearing lower than 1600 cm^{-1} [17, 18]. The vibrations of the imidazole ring, on the other hand, are expected to result in a weak combination band around 1665 cm^{-1} [9]. Namely, the bands originating from the internal vibrations of the heterocyclic bases are faithfully reproduced in the spectra of their adducts [19].

The single and very strong band at 1652 cm^{-1} in the RT infrared spectrum of the cadmium complex (Fig. 4A) can undoubtedly be assigned as $\nu(\text{CO})$ mode. At LNT (Fig. 5A), the maximum of the band is shifted to 1656 cm^{-1} , while the asymmetric shape of the band is more pronounced (at least one shoulder, around 1644 cm^{-1} , appears). Otherwise, as it is expected from the deprotonation of the saccharin molecule and the subsequent electron redistribution within the five-membered ring of the saccharinato ligand, the $\nu(\text{CO})$ frequency in the spectrum of the cadmium compound is lower than the corresponding frequency in the spectrum of saccharin itself (1725 cm^{-1}) [15].

The asymmetric shape of the $\nu(\text{CO})$ band at LNT (Fig. 5A) implies that it could be resulted by an overlap of at least two bands at very close frequencies. This seems even more hopeful if the existence of *two* non-equivalent carbonyl groups in the structure (one of which is involved in the coordination to the metal atom) is taken into account [4]. However, the earlier conclusion that the correlation of the number of crystallographically

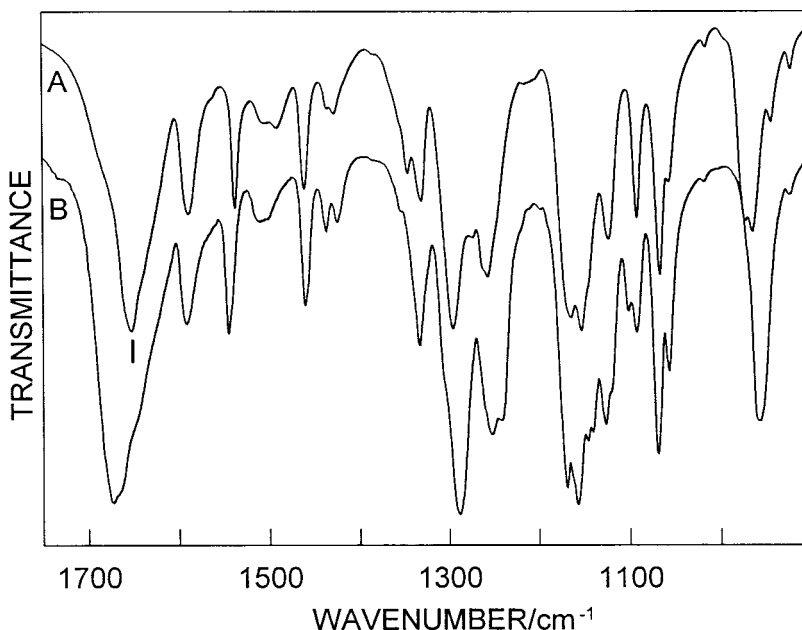


Fig. 4. RT Infrared Spectra of $[\text{Cd}_2(\text{HIm})_4(\text{sac})_4]$ (A) and $[\text{Cu}_2(\text{HIm})_4(\text{sac})_4]$ (B) in the $1750\text{-}900\text{ cm}^{-1}$ Region

independent carbonyl groups in the structure and the number of $\nu(\text{CO})$ bands in the spectrum is not always straightforward [14] should not be neglected.

The finding that the $\nu(\text{CO})$ bands in the case of the Cd complex are not resolved even at LNT could mean the existence of similar C-O distances between the two non-equivalent carbonyl groups in its structure. The frequency of the assigned $\nu(\text{CO})$ mode (1656 cm^{-1}) in the studied complex is considerably lower than that of the higher-frequency $\nu(\text{CO})$ band in the case of the Cu complex (1674 cm^{-1}) and at the same time, close to the frequency of the band prescribed to the bridging carbonyl group (1651 cm^{-1}) (Fig. 5). This could be an indication that, besides being close to each other, the C-O distances in cadmium imidazole saccharinate are similar to the longer C-O distance found in the copper compound [$122.3(5)\text{ pm}$] [3].

Compared to other saccharinates that feature coordination through a saccharinato carbonyl group, the $\nu(\text{CO})$ frequency of cadmium imidazole saccharinate is higher than the frequency of the corresponding mode in Na saccharinate (1635 cm^{-1}) and the mean value (1643 cm^{-1}) in Mg saccharinate (Table 1). This leads to expectation of somewhat

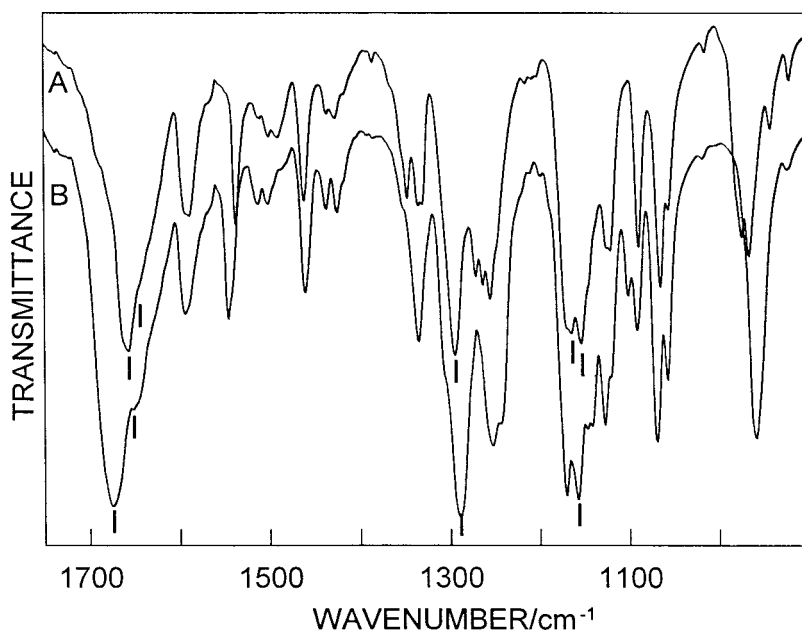


Fig. 5. LNT Infrared Spectra of $[\text{Cd}_2(\text{HIm})_4(\text{sac})_4]$ (A) and $[\text{Cu}_2(\text{HIm})_4(\text{sac})_4]$ (B) in the $1750\text{-}900\text{ cm}^{-1}$ Region

shorter C-O distances in the cadmium complex than those found in the saccharinates of Na and Mg. However, since the values of the C-O bond lengths are not given in the paper reporting the structure [4], at this stage the above predictions can not be confirmed by structural data.

As from the spectra-structural conclusions in a series of metal saccharinates follows, the frequency of the $\nu(\text{CO})$ mode can be used to make certain predictions on the type of metal-saccharin bonding [14, 15]. It was found, namely, that the lowering of the $\nu(\text{CO})$ frequency in metal saccharinates compared to the saccharin itself is more pronounced in the case of the ionic saccharinates than in the saccharinates where the metal-saccharinato bonds are mainly covalent. The $\nu(\text{CO})$ frequency in the spectrum of the cadmium imidazole saccharinato complex is lower than the frequency of the corresponding mode in the *covalently* bonded saccharinates of Hg(II) and ClHg(II), but higher, as it was mentioned previously, than in purely *ionic* saccharinates of Na, Mg and Pb(II) (Table 1). This might be an indication that the metal-saccharinato bonds in the studied compound has an *intermediate* character.

Table 1. Basic Structural and Spectroscopic Data Concerning the Carbonyl Groups in Some Metal Saccharinates

Compound	$R(\text{C-O})/\text{pm}$	$R(\text{C-O})_{\text{av}}/\text{pm}$	Frequency Data/ cm^{-1}	
			$\nu(\text{CO})$	$\nu(\text{CO})_{\text{av}}$
Hg(sac)₂ Ref. 14, 24	118(2) 120(2) 122(2) 123(2)	121	1680 1705	1692
HgCl(sac) Ref. 14, 25	123(2)	123	1694	1694
Pb(sac)₂·H₂O Ref. 26, 27	120.4(15) 125.5(15)	122.9	1601 1610	1605
Mg(sac)₂·7H₂O Ref. 28, 16	124.0(3) 124.2(3)	124.1	1627 1660	1643
Na₃(sac)₃·2H₂O Ref. 28, 15	123.0(3) 124.1(4) 123.7(3)	123.6	1635	1635
Cu₂(HIm)₄(sac)₄ Ref. 3, 6	110.3(6) 122.3(5)	116.3	1674 1651	1662
Cd₂(HIm)₄(sac)₄ [this work]	?	?	1656	1656

Sulphonyl stretching region

As it was shown [20], the stretching vibrations of the sulphonyl group can be considered as good group vibrations. The presence of other bands originating from the ligand internal modes in the same region in the spectra of the saccharinates, however, can often complicate the assignment of the bands arising from the $\nu(\text{SO}_2)$ modes [21]. According to the *ab initio* results for saccharin and the saccharinato nitranion [22] and the NCT results for phtalimide, potassium phtalimide and potassium tetrachlorophtalimide follows [17, 18], at least *five to six* bands originating from the saccharinato ligand can be expected in the $1345\text{-}1100\text{ cm}^{-1}$ region. It was an empirical conclusion, however, that

the sulphonyl stretching bands differ from the sharp benzenoid bands both by stronger intensity and by lower sensitivity to temperature changes. The NCT results for imidazole, on the other hand, predict *two* bands in this region, but *five* bands were actually found [9]. From the structural data for the studied complex [4] it follows that the sulphonyl groups are involved in intermolecular hydrogen bonding, which could additionally complicate the spectral appearance in this region.

At least *nine* bands with appreciable intensity can be seen in the 1345-1100 cm^{-1} region of the LNT spectrum of the studied complex (Fig. 5A). The strongest one among them, with a maximum at 1294 cm^{-1} , can undoubtedly be assigned as *asymmetric stretching* mode of the sulphonyl groups.

When the $\nu_s(\text{SO}_2)$ mode is concerned, however, it seems rather difficult to give a reliable assignment. Namely, similarly to the case of the copper complex (Fig. 5), two very strong bands in the 1200-1100 cm^{-1} region, at 1164 cm^{-1} and 1153 cm^{-1} , seem to be candidates for this assignment. The temperature-change shift of both bands is similar and can not be helpful in this sense. In absence of precise structural data, therefore, the assignment of a particular band to the actual mode would be rather tentative and will not be attempted here.

The frequencies of the sulphonyl stretching modes in the studied compound (1294 and 1164 or 1153 cm^{-1} for the asymmetric and the symmetric mode, respectively) are lower compared to the corresponding frequencies in the spectrum of saccharin itself (1335 and 1180 cm^{-1} [14]). This was found to be common for the previously studied saccharinates [21] and is probably due to the charge redistribution within the saccharinato ligand [22].

As shown in Table 2 and Figs. 4 and 5, the asymmetric SO_2 stretching in the spectrum of cadmium(II) imidazole saccharinate is similar in frequency with the corresponding modes in the spectra of Mn(II) saccharinate and Cu(II) imidazole saccharinate. Depending on the assignment of the symmetric stretching mode, however, the frequency difference between the two $\nu(\text{SO}_2)$ modes in the studied complex is similar or larger than that in the mentioned saccharinates (Table 2; Fig. 5). As from the spectra-structural correlations in metal saccharinates follows [21], this might be an indication of existence of

Table 2. Some Structural and Spectroscopic Data Concerning the Sulphonyl Groups in Some Metal Saccharinates

Compound	$R(\text{S-O})/\text{pm}$	$\angle(\text{OSO})/^\circ$	SO_2 Frequency Data/ cm^{-1} *					ν_s/ν_a
			ν_{as}	ν_s	Δ	Δ'	Δ''	
Na Refs. 14, 18, 21	144.3(2)	112.9(1)						
	145.0(2)							
	144.6(2)	113.9(1)	1260	1150	110	75	30	0.913
	145.6(2)							
	144.5(2)	114.0(1)						
	145.5(2)							
Mg Refs. 14, 18, 21	144.5(2)	114.4(1)						
	144.9(2)		1265	1155	110	70	25	0.913
	142.2(2)	114.4(1)						
	144.5(2)							
Mn(II) Refs. 14, 20	143.7(2)	116.1(1)	1288	1155	133	47	25	0.897
	144.5(2)							
Cu₂(HIm)₄(sac)₄ Ref. 3, 6	142.0(4)	113.3(3)						
	143.8(4)		1288	1157	131	43	23	0.898
	143.9(4)	115.4(3)						
	144.5(4)							
Cd₂(HIm)₄(sac)₄ [this work]	?	?	1294	1164 or 1153	130 or 141	41	16 or 27	0.899 or 0.891

* The values in the last column are dimensionless. The symbols denote:

$$\Delta = \tilde{\nu}(\nu_{\text{as}}) - \tilde{\nu}(\nu_s); \Delta' = \tilde{\nu}[\nu_{\text{as}}(\text{Hsac})] - \tilde{\nu}[\nu_{\text{as}}(\text{M-sac})]; \Delta'' = \tilde{\nu}[\nu_s(\text{Hsac})] - \tilde{\nu}[\nu_s(\text{M-sac})].$$

similar or somewhat larger O-S-O angles in the structure of Cd complex than those found in the Cu complex or Mn(II) saccharinate. Furthermore, considering the more pronounced difference between the $\nu(\text{SO}_2)$ modes in the studied complex than in the ionic saccharinates of Na and Mg (Table 2), it is even more likely to suppose [21] higher values for the O-S-O angles in Cd imidazole saccharinate.

Regardless to the assignment of the particular band to the symmetric stretching mode, only *one* pair of sulphonyl stretching bands appears in the spectrum of the studied compound (Fig. 5A), besides the presence of *two* non-equivalent sulphonyl groups in its structure [4]. This, however, is not surprising, considering that the number of structurally independent sulphonyl groups could not be always correlated with the number of pairs of $\nu(\text{SO}_2)$ bands [21]. As an example, besides the existence of *three* structurally different O-S-O angles in Na saccharinate [23], only *one* pair of bands attributable to the sulphonyl stretchings are found in its spectrum [16]. This was prescribed to the small difference among the values of the O-S-O angles (maximum difference of 1.1°). In spite of the expectation of two pairs of SO_2 bands corresponding to the *two* structurally different sulphonyl groups in copper imidazole saccharinate, only *one* pair of bands was in fact observed, which was also believed to be due to the close O-S-O angles (difference of 2.1°) [6]. It seems reasonable, therefore, to suppose that in spite of the existence of two structurally non-equivalent SO_2 groups in Cd imidazole saccharinate, the difference in the values of the O-S-O angles between them is rather small. However, since the accurate data pertaining to the sulphonyl groups in the studied compound are missing, no such structural evidence can be given at the moment.

CONCLUSIONS

The conclusions of the present analysis can be briefly summarized as it follows:

1. The imino groups in Cd imidazole saccharinate participate in stronger hydrogen bonds than those in the analogous Cu complex. From the temperature shifts shown by the $\nu(\text{NH})$ bands it follows that one of the imino groups in the studied compound is involved in highly bent hydrogen bonding. Vibrational interactions are probably responsible for the larger number of $\nu(\text{NH})$ bands observed in the spectrum of the Cd complex than the number of the non-equivalent imino groups found in its structure.

2. The lengths of the two non-equivalent carbonyl groups in the structure of the Cd complex are expected to be similar to each other and, in the same time, similar with the length of the longer carbonyl group in the Cu compound, but somewhat smaller than the

corresponding values in the saccharinates of Na and Mg. The character of the Cd-saccharinato bonds is found to be between ionic and purely covalent.

3. The values of the O-S-O angles in the studied compound should be similar or somewhat larger than the corresponding values in the structure of the Cu complex.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry for Science of the Republic of Macedonia for the financial support.

REFERENCES

1. J. Li, Y. Zhang, W. Lin, S. Liu, J. Huang, *Polyhedron*, **11**, 419 (1992).
2. Y. Zhang, J. Li, W. Lin, S. Liu, J. Huang, *J. Cryst. Spec. Res.*, **22**, 433 (1992).
3. S. Liu, J. Huang, J. Li, W. Lin, *Acta Crystallogr.*, **C47**, 41 (1991).
4. J. Li, Y. Ke, Q. Wang, X. Wu, *Cryst. Res. Technol.*, **32**, 481 (1997).
5. Y. Zhang, J. Li, *Spectrosc. Lett.*, **24**, 1395 (1991).
6. P. Naumov, G. Jovanovski, *Spectrosc. Lett.*, submitted for publication.
7. GRAMS/386 for Microsoft Windows, Version 2.02, Galactic Industries Corp., 1991-1993.
8. E. G. Ferrer, S. B. Etcheverry, E. J. Baran, *Monatsh. Chem.*, **124**, 355 (1993).
9. M. Cordes, L. J. Walter, *Spectrochim. Acta*, **A24**, 237 (1968).
10. J. W. Davis, J. Smith, *J. Chem. Soc., A*, 317 (1971).
11. B. J. Hodgson, C. G. Percy, A. D. Thornton, *Spectrochim. Acta*, **A35**, 949 (1979).
12. O. Knop, W. Westerhause, M. Falk, *Can. J. Chem.*, **58**, 867 (1980).
13. M. Majoube, *J. Mol. Struct.*, **61**, 129 (1980).
14. G. Jovanovski, B. Šoptrajanov, *J. Mol. Struct.*, **174**, 467 (1988).
15. G. Jovanovski, B. Šoptrajanov, B. Kamenar, *Bull. Chem. Technol. Macedonia*, **8**, 47 (1990).
16. G. Jovanovski, *Ph. D. Thesis*, University of Zagreb, 1981.
17. I. Hase, *J. Mol. Struct.*, **48**, 33 (1978).
18. I. Hase, *J. Mol. Struct.*, **52**, 163 (1979).
19. M. Goldstein, F. E. Monney, A. Anderson, A. H. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).
20. T. Uno, K. Machida, K. Hanai, *Spectrochim. Acta*, **A27**, 118 (1971).
21. G. Jovanovski, S. Tančeva, B. Šoptrajanov, *Spectrosc. Lett.*, **28**, 1095 (1995).
22. I. G. Binev, A. B. Stamboliyska, E. A. Velcheva, *Spectrochim. Acta*, **A52**, 1135 (1996).
23. G. Jovanovski, B. Kamenar, *Cryst. Struct. Commun.*, **11**, 247 (1982).
24. B. Kamenar, G. Jovanovski, Grdenić D., *Cryst. Struct. Commun.*, **11**, 263 (1982).
25. G. Jovanovski, B. Kamenar, G. Ferguson, B. Kaitner, *Acta Crystallogr.*, **C44**, 616 (1988).
26. A. Hergold-Brundić, B. Kamenar, G. Jovanovski, *Acta Crystallogr.*, **C45**, 556 (1989).
27. S. Tančeva, G. Jovanovski, B. Šoptrajanov, *Spectrosc. Lett.*, **25**, 927 (1992).
28. B. Kamenar, G. Jovanovski, *Cryst. Struct. Commun.*, **11**, 257 (1982).

Povzetek

Prikazani so FT-IR spektri protoniranega in iminodevteriranega kadmijevega(II) imidazol saharinato kompleksa pri sobni temperaturi in pri temperaturi tekočega dušika v spektralnem območju 4000-500 cm^{-1} . Trakovi v glavnem pripadajo valenčnim nihanjem imino, karbonilnih in sulfonilnih skupin. V diskusiji obravnavamo tudi področje NH in ND valenčnih nihanj. Na osnovi primerjave s podobno bakrovo(II) spojino in drugimi kovinskimi saharinami smo spektralno območje CO_2 in SO_2 valenčnih nihanj uporabili za določene strukturne napovedi.