

RAMAN SPECTRUM OF THE BINUCLEAR COPPER(II) IMIDAZOLE SACCHARINATO COMPLEX

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Abstract: The solid-state Raman spectrum of the binuclear copper(II) saccharinato adduct with imidazole (CuIMS), featuring the shortest C–O bond in all so far structurally characterized saccharinates, is recorded and comparatively studied with those of saccharin and other saccharinato compounds. The appearance of the regions of characteristic CO and SO₂ stretching vibrations is discussed. The Raman spectrum of the free saccharinato ion was computed for its HF/6-31++G(d,p) optimized geometry.

Two room-temperature Raman $\nu(\text{CO})$ bands (1669 and 1655 cm⁻¹) could be successfully resolved by the curve-fitting procedure, along with the existence of two structurally different carbonyl groups in CuIMS. Notable is that the ratio of the integral intensities of the two resolved $\nu(\text{CO})$ fundamentals in the infrared is appreciably different from the corresponding Raman value. The coordination and inclusion of the longer CO group in the centrosymmetric octagonal ring of the dimer were suspected to be responsible for such discrepancy.

1. Introduction

The room temperature (RT) X-ray crystal structure of the binuclear copper(II) imidazole saccharinate, [Cu₂(HIm)₄(sac)₄]¹ (CuIMS), was published in 1991 by Liu et al. [1]. During our recent exhaustive survey of the Cambridge Structural Database for the structural data on metal saccharinato salts and complexes [2] it revealed out that the title compound represents rather special case. Namely, while the length of the bridging carbonyl group in this compound is quite normal [122.3(5) pm], the non-bridging carbonyl group features the shortest C–O distance [110.3(6) pm] [1] in all so far structurally characterized saccharinates. Having in mind that the temperature factors of the carbonyl oxygen are quite comparable to those of the other atoms and the very short C–O distance is appropriated with very long (at least for the structures of saccharinates) adjacent C–N bond, we abandoned the initial presumptions about eventual disorder within the short carbonyl group in CuIMS. Alternative explanation was previously given by Zhang et al. [3], prescribing this unusually short bond to the so-called "space obstacle effect" of the carbonyl group with the neighboring imidazole ring.

In continuation of our spectra-structural investigations on metal saccharinates, we have recently discussed the characteristic regions of the FT IR spectrum of the title compound at liquid-nitrogen boiling temperature (LNT) [4]. In order to examine further the spectral characteristics of CuIMS, in the present communication we report its RT Raman spectrum. The assignment of the saccharinato vibrations is aided with the ab initio theoretical calculations on the free saccharinato ion performed at the HF/6-31++G(d,p) level.

¹ The acronym "HIm" denotes imidazole, while "sac" is used for saccharinato ligand or an ion.

2. Materials and Methods

2.1. Experimental

The copper complexes were prepared as described elsewhere [1, 4]. The identity of CuIMS was checked by the close proximity of the unrefined unit cell parameters obtained from 20 reflections in the 2θ range $15\text{--}30^\circ$ (collected with a STOE four-circle diffractometer at RT) with the published values [1], as well as by elemental analysis. The Raman spectra in the $1800\text{--}30\text{ cm}^{-1}$ region were recorded on a Renishaw 2000 instrument equipped with a Leica microscope, using a 514 nm argon-ion or a 780 nm diode lasers.

2.2. Theoretical calculations

The ab initio calculations were performed with the *Gaussian 94w* series of computer programs (the details are described in Ref. 5). Since we considered that the basis set 3-21G(d) used previously by Binev et al. [5] to compute the infrared spectrum of saccharin and its anion is rather small, we used the larger, but yet computationally feasible basis set 6-31++G(d,p) (diffuse functions were added to all atoms to obtain better description of the electronic structure of the negatively charged ion). Subsequent harmonic vibrational analysis furnished 42 normal modes (no imaginary frequencies were obtained), while the frequencies were scaled with the factor 0.92268 that was obtained as an average value from the calculated and observed frequencies of three very prominent saccharinato bands.

3. Results and Discussion

The recorded (solid state) Raman spectrum of CuIMS together with the calculated spectrum of the isolated saccharinato ion are shown in Fig. 1.

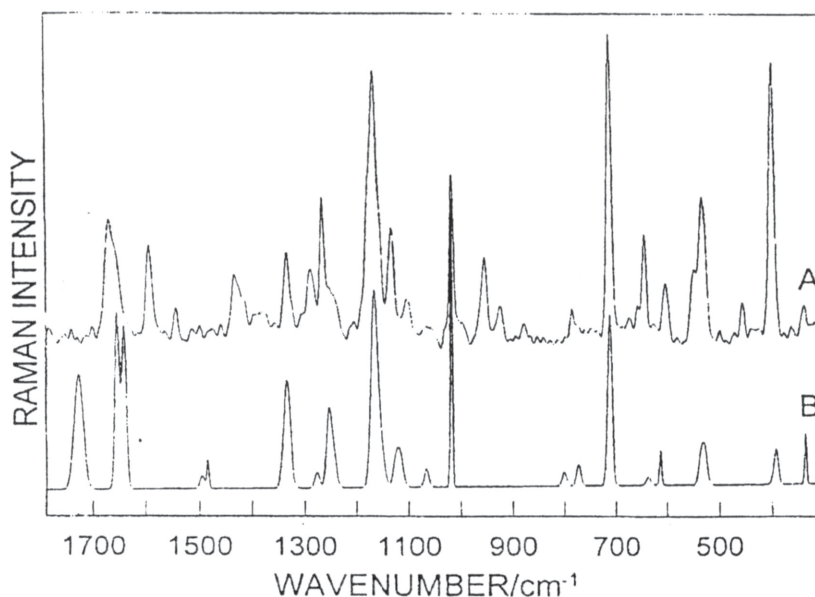


Fig. 1. Experimental Raman Spectrum of Cu(II) Imidazole Saccharinate (A) and the Theoretically Calculated Spectrum of the Saccharinato Ion (B)

3.1. Carbonyl Stretchings

Two component bands (1669 and 1655 cm^{-1} , hereafter denoted bands I and II, respectively) could be successfully resolved by the curve-fitting procedure (Fig. 2). Band I would correspond to the shorter, non-coordinated carbonyl group (CO group I), while band II is attributed to the longer, coordinated carbonyl group (CO group II). Although the assigned $\nu(\text{CO})$ modes have their counterparts at close frequencies in the LNT infrared (1674 and 1651 cm^{-1}) [4], notable is that the integral intensity ratio of the two resolved CO fundamentals in the IR (about 5.3) is far exceeding the corresponding Raman value (about 0.9). The mentioned small length of the CO group I could be intuitively taken as one (albeit probably not the only) factor that lowers the intensity of the band I in the IR. Contrary to the CO group I, on the other hand, CO group II is coordinated and included in the centrosymmetric octagonal ring and thus should be intensified in the Raman (in comparison with the most prominent bands in the spectrum). Bands I and II, therefore, should feature comparable intensities in the Raman, as it is indeed observed.

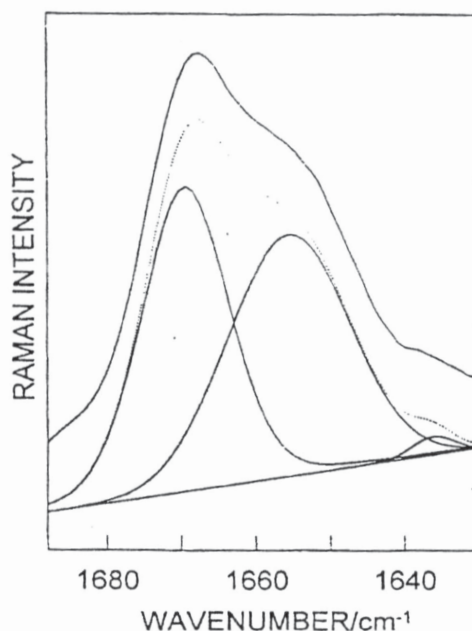


Fig. 2. Carbonyl Stretching Region in the RT Raman Spectrum of Cu(II) Imidazole Saccharinate (the uppermost curve) and the Corresponding Reconstructed Spectrum (dotted curve) (other curves represent the component bands)

Both the frequency differences of the Raman $\nu(\text{CO})$ modes of CuIMS (56 and 70 cm^{-1}) and of the corresponding IR values (51 and 74 cm^{-1}) from the IR saccharin value² show that the bidentate saccharinato ligand (II) is more ionically bonded to the metal atom than the monodentate one (I). This is supported by the structural data [1] revealing that the Cu-N(sac II) bond [$206.9(4)\text{ pm}$] is shorter than the Cu-N(sac I) bond [$211.3(4)\text{ pm}$]. In the present case,

² As it is found from the vibrational spectra of saccharin [6], the two carbonyl stretches of the saccharinato dimer in the solid state are strongly coupled, and thus the infrared $\nu(\text{CO})$ band corresponds with their antisymmetric stretching mode.

therefore, besides the dissimilarity of the structural environments of the two non-equivalent CO groups, the relative lengths of the Cu–N(sac) bonds *are* reflected on the frequencies of the $\nu(\text{CO})$ modes.

3.2. Sulfonyl Stretchings

The *antisymmetric* $\nu(\text{SO}_2)$ mode in the Raman spectrum of CuIMS is found as a weak band at very close frequency (1287 cm^{-1}) with that in the LNT IR (1288 cm^{-1}) [4] (Fig. 1).

Due to the presence of additional strong bands, however, the assignment of the *symmetric* $\nu(\text{SO}_2)$ mode in the LNT IR spectrum was troublesome [4]. From two candidates (1170 and 1157 cm^{-1}), the latter was tentatively assigned to this mode. As it was found in the case of alkali saccharinates [6], on the other hand, the $\nu_s(\text{SO}_2)$ mode(s) is(are) expected as rather strong band(s) in the Raman. The very prominent and asymmetric band at 1166 cm^{-1} in the Raman spectrum of CuIMS (Fig. 1), therefore, can be prescribed to this mode. It follows from there that it is very likely to assign the IR band at 1170 cm^{-1} , rather than the one at 1157 cm^{-1} to the symmetric $\nu(\text{SO}_2)$ mode.

4. Conclusions

In conclusion, the present study shows that, even within a single compound, the factors influencing the frequency and/or the intensity of the carbonyl stretching of the metal saccharinates are far more complex than the length of the carbonyl group alone. Understandably, furthermore, the assignment of the symmetric $\nu(\text{SO}_2)$ modes in rather complex structural systems, such are the various saccharinato salts and complexes, is more reliable if the corresponding Raman data are taken into account.

5. References

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РАМАНСКИ СПЕКТАР НА БИНУКЛЕАРНИОТ КОМПЛЕКС НА БАКАР(II) САХАРИНАТ СО ИМИДАЗОЛ

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Апстракт: Снимен е Раманскиот спектар (во цврста состојба) на бинуклеарниот комплекс бакар(II) имидазол сахаринат (CuIMS), што се карактеризира со најкуса C–O врска кај сите досега структурно изучени сахаринати и спореден е со спектрите на сахарин и други сахаринатни соединенија. Дискутиран е спектралниот изглед во областите на карактеристичните (CO и SO₂) валентни вибрации. Теориски е пресметан Раманскиот спектар за HF/6-31++G(d,p) оптимизираната геометрија на слободниот сахаринатен јон.

Во согласност со постоењето на две структурно различни карбонилни групи кај CuIMS, со реконструкција на спектарот, раздвоени се две Рамански ленти (1669 и 1655 cm^{-1}). Односот на интегралните интензитети на двете $\nu(\text{CO})$ ленти во инфрацрвениот спектар е многу различен од оној во Раманскиот. Некои од причините за ова би можеле да бидат координацијата и учеството на подолгата CO група во центросиметричниот осумчлен прстен на димерите.