Dedicated to Professor Dimče Tošev on the occasion of his 80th birthday

EXPERIMENTAL AND THEORETICAL FT INFRARED STUDY
OF BIS(ISATINATO)MERCURY(II):
CORRELATION WITH THE STRUCTURE

Panče Naumov and **Frosa Anastasova**

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, The "Sv. Kiril & Metodij" University, P.O. Box 162, MK–1001 Skopje, Republic of Macedonia
E-mail: spance@iunona.pmf.ukim.edu.mk

The 4000–400 cm^{-1} region of the Fourier transform infrared spectra of bis(isatinato)mercury(II), recorded at room and at low temperature, was studied together with that of isatin. Ab initio geometry optimization and vibrational analysis at the HF/6–31G(d,p) level were carried out on the isolated isatin molecule and the isatinato nitranion to give theoretical grounds to the assignments. Satisfactory agreement was found among theoretical and experimental spectroscopic and structural data concerning the carbonyl groups in the complex.

Key words: bis(isatinato)mercury(II); carbonyl stretchings; FT IR spectra

INTRODUCTION

Scientific interest in the structural properties of derivatives of isatin (commonly known as indoline-2,3-dione) and their complexes with various metals have evolved mainly from their biological activity [1, 2]. It was found, namely, that the structural properties of substituted isatins can be related with their biological activity. For instance, a recent quantitative structure-activity relationship study [3] showed that the biological activity (particularly, the anticarcinogenic action) of various substituted isatins is influenced by the nature of the substituent and the substitution atom of isatin. Having in mind that the biological activity of organic molecules is significantly altered and often enhanced by their complexation with metal ions, it is of interest to investigate the structural properties of metal complexes of isatin and its derivatives.

The crystal structure of isatin was determined as early as in 1950 [4], but due to the low accuracy of the data, it was independently redetermined later on by three groups of authors [5–7]. Contrary to

the parent molecule, not much detailed structural data exist on its metal complexes. The crystal and molecular structure of bis(isatinato)mercury(II) (denoted 'HgISA' henceforward) was recently reported [8] and it was pointed out as the first determined structure of metal(II) complex of isatin. The compound has been considered as a potential model for the metal-biomolecule interactions of mercury(II) with DNA.

Not much more prevalent are the spectroscopic data on isatin, its derivatives and complexes. There is a recent report on the NMR spectra of some cyano-substituted isatins [6] as well as on the ^{14}N quadrupole coupling constants of the parent molecule [9]. We have investigated the middle infrared region of both room and low-temperature vibrational spectra of some biologically active 5- [10] and *N*-substituted [11] isatins.

In the present paper we report the infrared spectrum of HgISA, compare it with the spectrum of the parent imide and attempt to correlate the

characteristic spectral and X-ray structural data. Besides being the only metal isatinate with known structure, this compound in addition features rather a simple crystal structure which offers some advantage to examine its infrared spectrum more quantitatively.

Description of the structure

Since a full description of the crystal structure of HgISA is given in Ref. 9, only the details that are relevant to the current discussion of the spectra will be briefly abstracted here. The compound crystallizes in the space group $P2_1/a$ of the monoclinic crystal system ($Z = 2$). The structure consists of polymeric chains that are parallel with the b axis of the unit cell and composed of structurally equivalent $Hg(C_8H_4NO_2)_2$ units (Scheme). Two deprotonated isatinato residues are diagonally *N*-

coordinated to a mercury(II) atom within each centrosymmetric $Hg(C_8H_4NO_2)_2$ unit. The neighboring units in the chain contact each other by interactions of $C–H\cdots O_{CO(amide)}$ type ($d(O\cdots H)$ = 244 pm) [9]. No π-aryl-mercury(II)-π-aryl stacking interactions were observed in the structure.
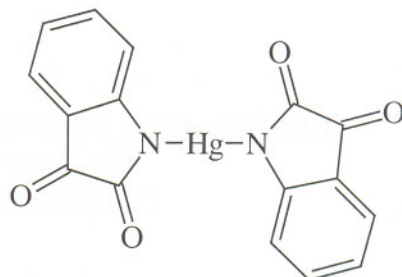
Scheme. Representation of a structural unit in bis(isatinato)mercury(II)

EXPERIMENTAL

Synthesis procedure

HgISA was synthesized from warm methanolic solution of Hg(II) acetate (Merck) and isatin (Merck) in stoichiometric ratio. Bright orange water-insoluble crystals were obtained from the solution after several days. The crystals were washed with methanol and dried in hood. The elemental analysis performed by standard analytical methods corresponded with the formula $Hg(C_8H_4NO_2)_2$ estimated by the diffraction experiment [1].

Recording of the spectra

The FT infrared spectra in the 4000–400 cm^{-1} frequency range were recorded with a System 2000 interferometer (Perkin–Elmer) at room (RT) and at the boiling temperature of liquid nitrogen (LNT). 32 background and 64 sample at resolution of 4 cm^{-1} were averaged. Since no differences were observed between the spectra recorded in KBr and paraffin oil, the spectra were recorded from KBr pellets. A P/N 21525 (Graseby Specac) variable-temperature cell with KBr windows was used for the low-temperature measurements.

Theoretical calculations

All calculations were performed with the *Gaussian 94/w* suite of programs [12]. Geometries of the free isatin molecule and the isatinato ion were initially optimized by the CNDO method and the resulting structures were further optimized at the Hartree-Fock SCF level analytically computing the energy derivatives with use of Berny's algorithm [13]. A satisfactorily large, but yet computationally feasible basis set (6–31 G(d,p)) was used. The obtained stationary points were checked for minimum with subsequent harmonic vibrational analysis yielding no imaginary frequencies. The vibrational frequencies, their intensities and the corresponding normal modes were calculated at the same level of theory. The raw frequencies between 4000 and 1200 cm^{-1} were scaled [14] with the factor 0.9262 obtained as an average from three prominent bands (calculated at 1728, 1571 and 1446 cm^{-1}) identified in the RT spectrum of HgISA (at 1604, 1459 and 1333 cm^{-1}, respectively). The theoretical frequencies of the bands below 1200 cm^{-1} were scaled with the factor 0.8144.

RESULTS AND DISCUSSION

General discussion

The 2000–400 cm^{-1} region in the Fourier-transform infrared spectra of HgISA and isatin together with the calculated spectrum of the free isatinato ion are shown in Fig.1. The relevant spectroscopic and structural data are summarized in Tables 1 and 2.

As can be inspected from Fig. 1 and Table 1, the appropriately scaled calculated spectrum of the isatinato nitranion exhibits a satisfactory resemblance of the spectrum of HgISA. Therefore, although the results of the present calculation would strictly apply to a gas-phase structure of an isolated gas-phase ion, they can nevertheless be of assistance in the assignment of the bands due to the internal isatinato vibrations in the infrared spectrum of solid-state HgISA.
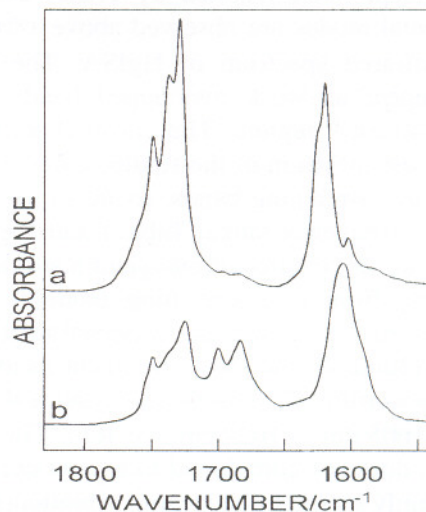

Fig. 1. The 1830–1540 cm^{-1} region in the LNT FT IR spectra of isatin (a) and bis(isatinato)mercury(II) (b)

Table 1

Experimental LNT FT IR spectroscopic data for bis(isatinato)mercury(II) (HgISA) and theoretically calculated data [6–31G(d,p)] for isolated isatinato anion

HgISA[a]	Frequency / cm^{-1} Isatinato ion		Intensity[c]	Approximate description[d]
	Unscaled	Scaled[b]		
2954w	3148	2916	38.4	
2919w	3131	2900	86.5	
2849w	3113	2883	47.2	ν(CH)
	3093	2865	8.7	
1724s	1864	1726	359.0	ν(CO)$_{ketone}$
1748m	1803	1670	25.6	ν(CC), ν(CO)$_{amide}$, δ(CCC)
1699m				
1683m	1758	1628	475.4	ν(CO)$_{amide}$, ν(CC), δ(CCC)
1605vs	1728	1600	508.0	ν(CC), δ(CCC), δ(CCN)
1474w	1629	1509	62.0	δ(CCC), ν(CC)
1460m	1571	1455	155.9	
1338m	1446	1339	225.8	δ(CCC), δ(CH)
1307m				
1276w	1355	1255	75.0	δ(CH)
1219m	1309	1212	91.1	
1192w	1283	1188	73.0	δ(CH), δ(CCC)
1151w	1218	1128	107.3	δ(CH), δ(CCC), ν(CC)
1120vw				
1093w				
973w	1182	963	244.3	δ(CH), ν(CC), ν(CN)
950vw	1150	937	0.9	
924w	1136	925	1.3	γ(CH)
918w	1111	905	24.9	δ(CH), δ(CCC)
905w	1092	889	437.0	δ(CH), δ(CCC)
870vw	1010	822	10.9	γ(CH)
817vw	1003	817	54.8	δ(CO), δ(CCN), δ(CC)[e]

[a] The acronyms denote: vs – very strong, s – strong, m – medium, w – weak, vw – very weak; [b] The values of the scaling factor are 0.9262 and 0.8144 for the bands with calculated frequencies higher and lower than 1200 cm^{-1}, respectively; [c] Calculated IR intensities (in km·mol^{-1}); [d] According to the shifts from the optimized atomic positions. The symbols denote: ν – stretching, δ – in-plane deformational, γ – out-of-plane deformational; [e] Followed by 17 lower-frequency modes.

Along with the calculations (Table 1), no bands except those resulted by ν(CH) and non-fundamental modes are observed above 1800 cm^{-1} in the infrared spectrum of HgISA. The ν(CH) bands appear as weak overlapped bands in the 2960–2840 cm^{-1} region. The most characteristic bands in the spectrum of the studied compound are the carbonyl stretching bands, found in the 1770–1650 cm^{-1} frequency range (Table 1 and Fig. 1). In addition, ab initio calculations yield a strong band originating from ring stretching mode(s) in the same region. Along with the expected relative intensities (Table 1), the most prominent band in the infrared spectrum of the isatinato ligand is the LNT band at 1605 cm^{-1} (1604 cm^{-1} at RT). This band, however, does not correspond to a carbonyl mode, but is mainly owing to benzenoid vibration(s). The corresponding mode in the LNT spectrum of isatin itself is found as a strong band at 1611 cm^{-1} (Fig. 1). The frequency decrease of this band accompanying the isatin mercuration confirms the presumptions [10] that the band is not due solely to benzene ring stretching, but includes contributions from vibrations localized in the five-membered ring. The vibrational analysis (Table 1) showed that the vibration corresponding to this band would be better described as ν(CC) + δ(CCC) + δ(CCN). Several bands of medium intensity appearing below 1500 cm^{-1} belong to coupled ring or CH in-plane deformational modes, being shifted and/or splitted in comparison with the corresponding isatin bands (Fig. 1). The CH out-of-plane deformations are observed as weak bands below 1000 cm^{-1}.

Carbonyl stretching region

A complex of strong bands with three maxima (1748, 1736 and 1727 cm^{-1}) is present in the ν(CO) region (1800–1650 cm^{-1}) of the LNT infrared spectrum of solid-state isatin (Figs. 1 and 2). From the harmonic vibrational analysis on the HF/6-31G(d,p) optimized structure of isolated isatin molecule a split of only about 9 cm^{-1} is expected between the two carbonyl modes (Table 2). Having in mind the usual appreciable halfwidth of the ν(CO) bands in the solid-state spectra, this expectedly small split between the two ν(CO) bands should be one of the factors contributing to their overlap and a consequent complex appearance of this spectral region.

At least four prominent and overlapped bands are present in the 1760–1650 cm^{-1} region of the LNT spectrum of HgISA (Fig. 2). However, the highest-frequency band in this region (1748 cm^{-1}) is also present in the spectrum of isatin and its position is unaltered upon mercuration. It might be, in fact, that the band is originally much weaker than the other bands in this region, but gains much of its intensity upon the overlap with the strong neighboring ν(CO) band. Moreover, in contrast with what is known for the ν(CO) modes, the band is insensitive to temperature changes. Having all this in mind, it does not seem probable that this band is mainly due to a carbonyl stretching. Indeed, the theoretical calculations (Table 1) predict the appearance in this region of a weak benzenoid band with only a minor contribution from the stretching mode of the amide CO group.
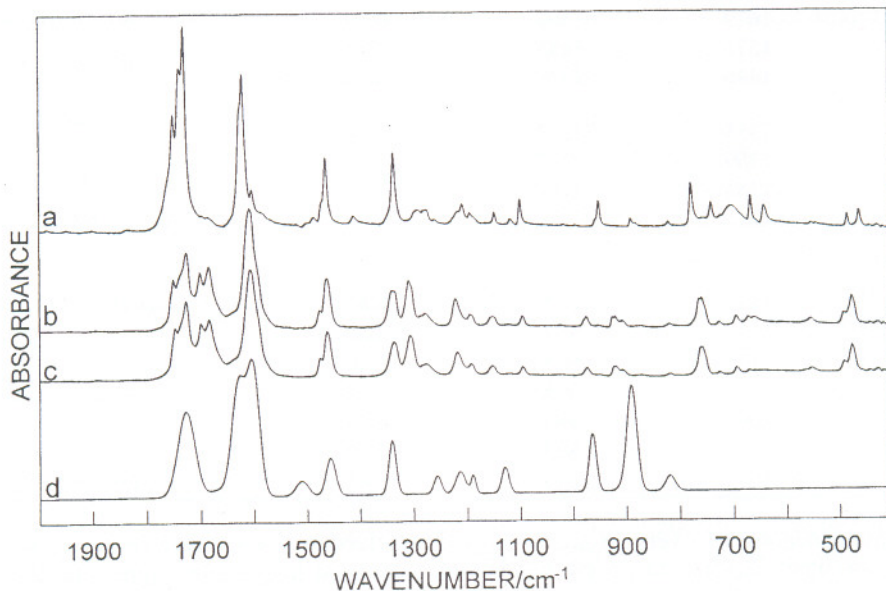

Fig. 2. The 2000–400 cm^{-1} region in the LNT spectrum of isatin (a), LNT (b) and RT (c) spectra of bis(isatinato)mercury(II) and the calculated spectrum of the isatinato ion (d)

The doublet of overlapped isatin ν(CO) bands (1736 and 1727 cm^{-1}) is replaced in the spectrum of HgISA by a single strong band (1724 cm^{-1}) with a shoulder on its higher-frequency side (Fig. 2). This band corresponds to the fairly pure stretching mode of the ketone carbonyl group in HgISA, in agreement with the ab initio results (Table 1). A pair of medium strong bands with similar intensities that appear at 1699 and 1683 cm^{-1} in the LNT spectrum of HgISA, on the other hand, can be prescribed to the stretching mode of the amide carbonyl group, i.e. the CO group adjacent to the nitranionic center. This vibration, however, is not as pure as ν(CO)$_{ketone}$ and involves contribution from ring modes (Table 1).

A general characteristic of the ν(CO) bands in the spectrum of HgISA is that their average frequency (1702 cm^{-1}) is lower than that of the ν(CO) bands in the spectrum of isatin (1731 cm^{-1}). The lowering of the isatin ν(CO) bands that follows the H/Hg substitution is expected consequence of the mass effect on the vibrations. The mass effect and the pronounced lowering of both carbonyl stretchings is also responsible for the order of frequencies observed in the spectrum of HgISA (ν(CC) > ν(CO)$_{ketone}$ > ν(CO)$_{amide}$) instead of what is expected for the isolated isatinato anion (ν(CO)$_{ketone}$ > ν(CC) > ν(CO)$_{amide}$) (Table 1). Furthermore, the experimental frequency difference (36 cm^{-1}) between the mean value of the two amide ν(CO) bands (1691 cm^{-1}) and the corresponding isatin mode (1727 cm^{-1}) is three times larger than the one in the case of the ketone ν(CO) mode (12 cm^{-1}). In other words, the shift of the amide ν(CO) bands towards lower wavenumbers upon mercuration is more pronounced than that of the ketone ν(CO)

bands. This, however, is understandable from the relative proximity of the two CO groups to the metalation center.

The appearance of two amide ν(CO) bands as well as of a band and a shoulder corresponding to the ketone ν(CO) mode does not seem to ally with the presence of only *two* crystallographic types of carbonyl groups in HgISA [8]. Some explanation on such spectral picture can be obtained by reference to the theoretical results presented in Table 1. As it was already mentioned, namely, the amide carbonyl stretching vibration in the deprotonated form of isatin is largely coupled with other modes. As a result to these "intrinsic" reasons, as well as to other (e.g., symmetry or solid-state) factors, more than one band with similar intensities involving contribution from the amide ν(CO) mode may appear in the spectrum.

Optimized parameters and spectra-structure correlations

From the basic structural and spectroscopic data concerning the carbonyl groups in isatin and HgISA listed in Table 2 it can be inferred that the spectroscopic data for the ν(CO) modes are generally in agreement with the predicted and experimentally observed C–O distances; i.e., *shorter* C–O distances correspond to *higher* ν(CO) frequencies. The difference between the calculated lengths of the two carbonyl groups in isatin, however, is negligible and it is apparent that in this case the theoretical results significantly underestimate both experimental values of the C–O lengths as well as the length difference between the two CO groups.

Table 2

Structural and spectroscopic data on the carbonyl groups in isatin and isatinato ion

Parameter	Isatin		Isatinato ion/ligand	
	Ab initio[a]	Experimental	Ab initio[a]	Experimental
$d(C-O)_{ketone}$ / pm	118.3	121.3(3) [7]	119.6	120.3(8) [8]
$d(C-O)_{amide}$ / pm	118.4	122.0(3) [7]	120.6	121.5(8) [8]
$\tilde{v}[\nu(CO)_{ketone}]$ / cm^{-1}	1917	1736	1726	1724
$\tilde{v}[\nu(CO)_{amide}]$ / cm^{-1}	1908	1727	1628	1699 1683

[a] The frequencies are scaled with the empirical factor 0.9262.

CONCLUSIONS

The two carbonyl stretching vibrations of isatin are separated and shifted to lower frequencies upon mercuration, the amide one being about three times more shifted than the ketone one. The coupling of the amide $\nu(CO)$ mode is accordingly enhanced, resulting in its splitting in two almost equally intense bands. Due to the mass effect on the carbonyl stretchings, the observed order of frequencies in the $\nu(CO)$ region of the spectrum of bis(isatinato)mercury(II) is $\nu(CC) > \nu(CO)_{ketone} > \nu(CO)_{amide}$ instead of the expected $\nu(CO)_{ketone} > \nu(CC) > \nu(CO)_{amide}$ for the free isatinato ion. An agreement was found between the theoretical and the experimental spectroscopic and structural data concerning the carbonyl groups.

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Р е з и м е

ЕКСПЕРИМЕНТАЛНО И ТЕОРИСКО ИЗУЧУВАЊЕ НА ФУРИЕОВИОТ ТРАНСФОРМЕН ИНФРАЦРВЕН СПЕКТАР НА БИС(ИЗАТИНАТО)ЖИВА(II): КОРЕЛАЦИИ СО СТРУКТУРАТА

Панче Наумов и Фроса Анастасова

Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј", п. фах 162, МК–1001 Скопје, Република Македонија E-пошта: spance@iunona.pmf.ukim.edu.mk

Клучни зборови: бис(изатинато)жива(II); карбонилни валентни вибрации; Фуриеови трансформни инфрацрвени спектри

Изучена е областа 4000–400 cm^{-1} од Фуриеовиот трансформен инфрацрвен спектар на бис(изатинато)-жива(II), снимен на собна и на ниска температура, заедно со дел од спектарот на изатинот. Со цел да се даде теориска интерпретација на спектарот на комплексот, направени се HF/6-31G(d,p) геометриска оптимизација и вибрациона анализа на изолирана молекула изатин и на изатинатниот нитранјон. Во однос на карбонилните групи во комплексот, најдена е задоволителна согласност помеѓу теориските и експерименталните спектроскопски и структурни податоци.