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Original Scientific Paper

Structural Investigation of Di-μ-chloro-bis[saccharinatopyridinemercury(II)] by X-ray Diffraction and FT IR Spectroscopy*

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The solid state structure of $[C_{12}H_9ClHgN_2O_3S]_2$ was determined and the appropriate assignment of the CO and SO_2 stretching vibrations in the FT IR spectrum was made. Two monomeric chlorosaccharinatopyridinemercury(II) moieties are joined together forming a di-μ-chloro bridged dimmer by an inversion centre operation. The mercury atom is coordinated with two bridging chlorine and the pyridine and saccharinato nitrogen atoms in the shape of a heavily distorted tetrahedron. There is a significant difference between Hg1–Cl1 [2.533(2) Å] and Hg1–Cl1^{i} [2.715(2) Å] distances as well as between Hg1–N11 [2.106(7) Å] and Hg1–N21 [2.209(7) Å] bond lengths. The valence bond angles at the metal atom deviate significantly from the standard tetrahedral value, ranging from 86.23(7)° for Cl1–Hg1–Cl1^{i} to 131.5(3)° for N11–Hg1–N21. Discrete molecules are linked together by weak *inter*molecular C–H$\cdots$O attractions at distances less than 3.5 Å.

Key words: chloromercury(II) saccharinate, pyridine adduct, X-ray structure determination, FT IR spectroscopy.

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[*] Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

Saccharin (systematic name: 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide) is one of the cyclic imides commonly used as a sweetening agent. Mainly due to the effectiveness of saccharin and its metal complexes in biological systems, extensive investigations have been done in this field during the last several decades. Namely, the chemical, structural and spectroscopic properties and especially physiological and biochemical activity of saccharin and its metal complexes have been studied. On the other hand, it has been shown that saccharin exhibits versatile coordination characteristics as a ligand with various metal cations. Among the complexes, the metal saccharinato compounds containing aromatic nitrogen bases as a second ligand have provoked certain attention.[1–4]

In order to obtain more information about the ligation properties of saccharin in the presence of other ligands, we have undertaken a systematic structural and spectroscopic study of saccharinate adducts with various mono- and polymembered ring nitrogen aromtic bases.[5–8] In this paper, we report the results of investigations of the pyridine complex of chloromercury(II) saccharinate by the methods of X-ray diffraction and FT infrared spectroscopy.

EXPERIMENTAL

Synthesis and IR Spectroscopy

$[HgCl(py)(sac)]_2$, (py stands for pyridine, sac denotes saccharinato ligand) was prepared for the first time by successive addition of equimolar quantities of pyridine and mercury(II) chloride to an aquous solution of sodium saccharinate. The mixture was continuously stirred for 30 minutes. Colourless prismatic crystals were grown by repeated crystallization from ethanol.

The infrared spectra were recorded at liquid nitrogen temperature (LNT) on a Perkin-Elmer System 2000 FT interferometer in the 4000–400 cm^{-1} region. The samples were recorded using KBr discs or Nujol mulls. For LNT measurements, a variable temperature cell P/N 21525 (Graseby Specac) with KBr windows was used.

*X-ray Diffraction Data Collecting and Processing**

Data were collected with a Philips PW1100 diffractometer using the ω scan method and graphite monochromatized Mo-Kα radiation. Details of the X-ray diffraction experiment and the refinement data are given in Table I. Three types of ab-

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* Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223–336033; e-mail: deposit@ccdc.cam.ac.uk) and can be obtained on request, free of charge, by quoting the publication citation and the deposition number 101448.

TABLE I

Summary of the general, X-ray diffraction and refinement data for di-μ-chloro-bis[saccharinatopyridinemercury(II)]

Molecular formula	$[C_{12}H_9ClHgN_2O_3S]_2$
Formula weight	994.64
Crystal shape and colour	prism, colourless
Crystal size / mm	$0.65 \times 0.57 \times 0.57$
Crystal system and space group	Monoclinic, $I2/a$[a]
Unit cell parameters[b]	
a / Å	14.590(2)
b / Å	12.357(2)
c / Å	15.300(2)
β / °	92.09(1)
Volume / Å^3	2756.6(7)
Unit cell content, Z	4
$F(000)$	1856
Calculated density, D_x / g cm^{-3}	2.397
Diffractometer	Philips PW1100
X-ray wave length, λ(Mo-Kα) / Å	0.7107
Data collection range and scan mode	$4° < 2\theta < 54°$; ω
Reflections measured[c]	3128
Independent reflections [$R_{int} = 0.043$]	3011
Linear absorption coefficient, μ(Mo-Kα) / mm^{-1}	11.52
Min. and max. transmission factors	0.0066; 0.0318
Observed reflections, $I_{net} \geq 2\sigma I_{net}$	2148
Residual, R	0.039
Weighted residual, wR	0.110
$[w^{-1} = \sigma^2(F_o^2) + (0.0795P)^2 + 16.2888P]$; $P = (F_o^2 + 2F_c^2) / 3$	
Goodness-of-fit, S	1.043
Extinction coefficient	0.00062(11)
Max. and min. electron densities in the last δF-map (e / Å^3)	–1.42; 1.44
Variables refined	182
Max. variable schift / error ratio	0.003
No. reflections / no. variables ratio	11.8

[a] *The International Tables for X-ray Crystallography*[13] standard $C2/c$ space group with unit cell parameters: $a = 20.753$ Å, $b = 12.357$ Å, $c = 14.590$ Å, $\beta = 132.54°$ has been transfered to the $I2/a$ non-standard setting one using the matrix transformation {0, 0,–1; 0, 1, 0; 1, 0, 1}.

[b] The unit cell dimensions were obtained by fitting the setting angles of 33 general reflections with $24° < 2\theta < 35°$.

[c] Four general strong standard reflections monitored every 90 minutes showed a ± 2% variation in the intensity during the data collection.

sorption corrections were applied to the data set. The numerical Gaussian method had to be rejected because no improvements in refinement procedure were observed.[9] The application of the semi-empirical ψ-scan and empirical absorption corrections based on the best isotropic model improved the refinement and reduced significantly the residuals in the difference Fourier map.[10,11] The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with all non-hydrogen atoms allowed anisotropic motion. Hydrogen atoms were positioned geometrically 0.95 Å from the atom to which they were bonded and included (but not refined) in the final rounds of calculations. The weights used in the refinement were based on counting statistics. Examination of the structure with PLATON showed that there were no solvent accessible voids in the lattice.[12]

Cell refinement, data collection and reduction, and ψ-scan absorption corrections: STADI4, X-RED and EMPIR.[14–16] Programs used to solve the structure: NRCVAX and SHELXL97.[17,18] Molecular graphics: ORTEP-III.[19] Software used to prepare material for publication: NRCVAX-Tables. All calculations were performed on a personal computer.

RESULTS AND DISCUSSION

Crystallographic Data

Final fractional coordinates are given in Table II and the details of geometrical dimensions are summarized in Table III. A perspective ORTEP-III[19] view of the molecule is depicted in Figure 1.

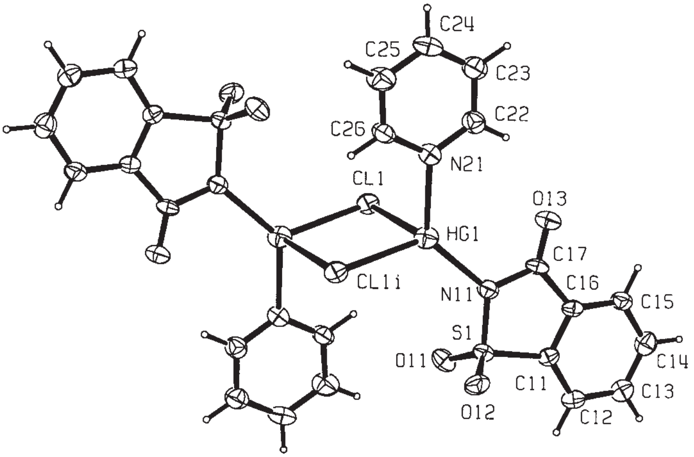

Figure 1. An ORTEP-III perspective view of the di-μ-chloro-bis[saccharinatopyridinemercury(II)] molecule in general orientation showing the atom numbering scheme. The non-hydrogen atoms are represented by 30% probability of vibrational ellipsoids. Hydrogen atoms are shown as open spheres of arbitrary radius. Label (i) refers to the -*x*, -*y*, -*z* equivalent position.

TABLE II

Final fractional atomic positional parameters for non-hydrogen atoms and equivalent isotropic thermal coefficients, U_{eq} / Å^2

Atom	x	y	z	U_{eq}
Hg1	0.09655(2)	0.10523(3)	0.00131(3)	0.0534(2)
Cl1	–0.0580(2)	0.0619(2)	0.0886(2)	0.0497(5)
S1	0.0406(2)	0.3016(2)	–0.1438(1)	0.0418(5)
O11	–0.0560(4)	0.2781(6)	–0.1432(4)	0.055(2)
O12	0.0875(6)	0.2620(6)	–0.2166(5)	0.061(2)
O13	0.1667(5)	0.3320(6)	0.0689(4)	0.056(2)
N11	0.0905(5)	0.2624(6)	–0.0518(5)	0.047(2)
C11	0.0621(6)	0.4403(6)	–0.1249(5)	0.039(2)
C12	0.0357(6)	0.5281(7)	–0.1758(6)	0.050(2)
C13	0.0585(7)	0.6292(8)	–0.1433(7)	0.054(2)
C14	0.1047(7)	0.6420(8)	–0.0650(7)	0.058(2)
C15	0.1314(7)	0.5523(7)	–0.0147(6)	0.049(2)
C16	0.1097(5)	0.4504(7)	–0.0468(5)	0.037(2)
C17	0.1276(6)	0.3449(7)	–0.0010(5)	0.040(2)
N21	0.1836(5)	0.0349(6)	0.1080(5)	0.046(2)
C22	0.2274(7)	0.0960(8)	0.1681(6)	0.054(2)
C23	0.2755(7)	0.0520(8)	0.2391(7)	0.061(3)
C24	0.2763(6)	–0.0570(8)	0.2478(6)	0.057(2)
C25	0.2312(8)	–0.1217(9)	0.1863(7)	0.069(3)
C26	0.1834(7)	–0.0728(8)	0.1180(6)	0.053(2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.

The structure is built up of discrete molecules linked together with weak C–H···O *inter*molecular electrostatic attractions shorter than 3.5 Å (Table IV).[20] The mercury atom completes its coordination sphere by dimmerization of two chloropyridinemercury(II) saccharinate monomeric units forming a di-μ-chloro bridged complex with an imposed crystallographic centre of inversion. Each metal atom is surrounded with two chlorine atoms as well as one pyridine and one saccharinato nitrogen atom, forming a severely distorted tetrahedral arrangement. Two tetrahedra share one edge, consisting of two bridging chlorine atoms.

The central Hg_2Cl_2 moiety is characterized by the significant difference in the mercury-to-chlorine bond length [2.533(2) and 2.715(2) Å]. Similar

TABLE III

Molecular geometry parameters

Valence bond lengths / Å			
Hg1-Cl1	2.533(2)	C12-C13	1.380(13)
Hg1-Cl1^{i}	2.715(2)	C13-C14	1.363(15)
Hg1-N11	2.106(7)	C14-C15	1.397(14)
Hg1-N21	2.209(7)	C15-C16	1.384(12)
S1-O11	1.439(7)	C16-C17	1.498(11)
S1-O12	1.416(7)	N21-C22	1.333(12)
S1-N11	1.635(7)	N21-C26	1.340(12)
S1-C11	1.765(8)	C22-C23	1.384(11)
O13-C17	1.204(9)	C23-C24	1.354(11)
N11-C17	1.381(10)	C24-C25	1.382(11)
C11-C16	1.366(11)	C25-C26	1.374(10)
C11-C12	1.381(11)		
Valence bond angles / °			
Cl1-Hg1-Cl1^{i}	86.23(7)	C11-C12-C13	116.7(8)
Cl1-Hg1-N11	110.4(2)	C12-C13-C14	121.8(9)
Cl1-Hg1-N21	91.4(2)	C13-C14-C15	120.7(10)
Cl1^{i}-Hg1-N11	122.5(2)	C14-C15-C16	118.1(8)
Cl1^{i}-Hg1-N21	101.0(2)	C11-C16-C15	119.7(7)
N11-Hg1-N21	131.5(3)	C11-C16-C17	113.9(7)
Hg1-Cl1-Hg1^{i}	93.77(7)	C15-C16-C17	126.3(7)
O11-S1-O12	115.9(4)	O13-C17-N11	124.4(8)
O12-S1-N11	111.2(4)	O13-C17-C16	126.9(8)
O11-S1-N11	109.9(4)	N11-C17-C16	108.7(6)
O11-S1-C11	111.3(4)	Hg1-N21-C22	122.3(6)
O12-S1-C11	112.1(4)	Hg1-N21-C26	118.1(6)
N11-S1-C11	94.4(4)	C22-N21-C26	119.1(8)
Hg1-N11-S1	128.1(4)	N21-C22-C23	122.4(9)
Hg1-N11-C17	117.0(5)	C22-C23-C24	118.0(9)
S1-N11-C17	114.8(5)	C23-C24-C25	120.4(9)
S1-C11-C12	128.8(7)	C24-C25-C26	118.6(9)
S1-C11-C16	108.3(6)	N21-C26-C25	121.4(9)
C12-C11-C16	122.9(8)		

Symmetry code: (i) *–x, –y, –z*.

TABLE IV

*Inter*molecular C–H···O hydrogen bonds less than 3.5 Å

D–H···A	d(D···A) / Å	d(H···A) / Å	∠ (D–H···A) / °
C13–H13···O12[i]	3.390(1)	2.598	140.99
C22–H22···O12[ii]	3.259(1)	2.905	103.41
C23–H23···O12[iii]	3.301(1)	2.756	117.29
C23–H23···O13[iv]	3.349(1)	2.481	151.90
C25–H25···O11[v]	3.253(1)	2.837	107.59
C26–H26···O11[v]	3.177(1)	2.643	116.06

Symmetry operators: (i) $-x$, y + 0.5, $-z$ – 0.5; (ii) x, $-y$ + 0.5, z + 0.5; (iii) $-x$ + 0.5, y, $-z$; (iv) $-x$ + 0.5, $-y$ + 0.5, $-z$ + 0.5; (v) $-x$, $-y$, $-z$.

Hg–Cl bond length discrepancy [2.500(4) and 2.742(3) Å] appears in the structure of Hg(II) chloride complex with 2-(2'-pyridyl)quinoxaline containing the same Hg_2Cl_2 bridging fragment.[21] There are cases, however, when the differences between the Hg–Cl distances in the Hg_2Cl_2 fragment are smaller [2.560(5) to 2.670(5) Å][22] or larger [2.317(8) and 3.240(8) Å].[23] A significantly shorter Hg–Cl bond length of 2.263(3) Å is found in the structure of chloromercury(II) saccharinate where the chlorine atoms are terminal.[24]

The slight difference between Hg–Nsac [2.106(7) Å] and Hg–Npy [2.209(7) Å] bond distances is related to the type of N-donor ligands as well as to the coordination pattern of the mercury atom. Accordingly, the Hg–Nsac bond length in the title compound, with tetrahedrally coordinated Hg atom, is longer compared to those found in chloromercury(II) saccharinate [2.021(8) Å][24] and mercury(II) saccharinate [2.03(1) to 2.06(1) Å][25] where the Hg atom has digonal characteristic coordination.[26] The Hg–Nsac distances [2.141(4) and 2.120(4) Å] in the structure of the 2,2'-bipyridine complex of mercury(II) saccharinate are very close to the corresponding value in the studied complex while the Hg–Nbpy bond lengths are expectedly longer [2.393(3) and 2.328(4) Å][5] than the Hg-Npy value found in the title compound. In the complexes with the larger *N,N*-bidendate chelate ligands coordinated with the mercury atom, the Hg–N bond lengths are also expectedly longer [2.480(4) and 2.336(10) Å][21] and [2.80(3) Å].[23]

The angles of the coordination polyhedron deviate considerably from ideal tetrahedral angles, the minimum value for $Cl–Hg–Cl^i$ amounting to 86.23(7)° and maximum value for Npy–Hg–Nsac being 131.5(3)°. Saccharinato ligand is planar within the experimental errors. Bond lengths and angles in this ligand are close to the values found in mercury(II) saccharinate,[25] chloromercury(II) saccharinate[24] and mercury(II) 2,2'-bipyridine saccharinate.[5]

IR Spectral Data

The infrared spectrum of the title compound was studied in the region of the CO and SO_2 stretching vibrations. Its spectral characteristics were compared with the corresponding ones in other mercury saccharinates.

Spectra–Structure Correlations

CO Stretchings

The bands that are due to the CO stretching vibrations appear in the region where modes mainly localized in the six-membered ring of the saccharinato[27,28] and pyridine ligand[29] are present (see also Figure 2). In the case of solid hydrates, bands arising from the HOH bending vibrations are also expected,[30,31] but if the compound is unhydrous, the bands belonging to the CO stretching vibrations dominate in the 1700–1600 cm^{-1} region. Like in the spectra of other mercury saccharinates, the benzenoid stretching bands appear at somewhat lower frequencies, being sharper and less intense than the bands originating from the CO stretches.

Having all this in mind, the strong single band at 1686 cm^{-1} in the LNT spectrum of the title compound (Figure 2B) could, beyond doubt, be attributed to the CO stretching mode. The appearance of a single band in this region is in agreement with the existence of one type of saccharinato ligand in the structure. The frequency of the CO stretch in the spectrum of the title compound (1686 cm^{-1}) is lower than the frequency of the corresponding mode for the saccharin itself (1725 cm^{-1})[7] but similar to those found for the other two covalently bonded mercury saccharinates, $Hg(sac)_2$ (1705 and 1680 cm^{-1}) and HgCl(sac) (1694 cm^{-1}).[7]

Although, in principle, the correlation between the CO stretching frequencies and the C–O distances for the metal saccharinates is not very accurate,[31] it seems that, in the cases of HgCl(sac) and $[HgCl(py)(sac)]_2$, the structural data concerning the CO group are in a fairly good agreement with the frequency range for the CO stretch (Table V). Namely, the slightly shorter C–O distance in the structure of $[HgCl(py)(sac)]_2$ is in agreement with the somewhat higher frequency for the stretching CO mode, as compared to the corresponding values for HgCl(sac).

SO_2 Stretchings

It is widely accepted that the sulphonyl stretching modes are characteristic group vibrations.[32–35] The assignment of the bands originating from the SO_2 stretching vibrations in the spectra of saccharinato salts and complexes is usually accompanied with difficulties due to the fact that additional bands, originating from ring vibrations of the saccharinato ligands, are

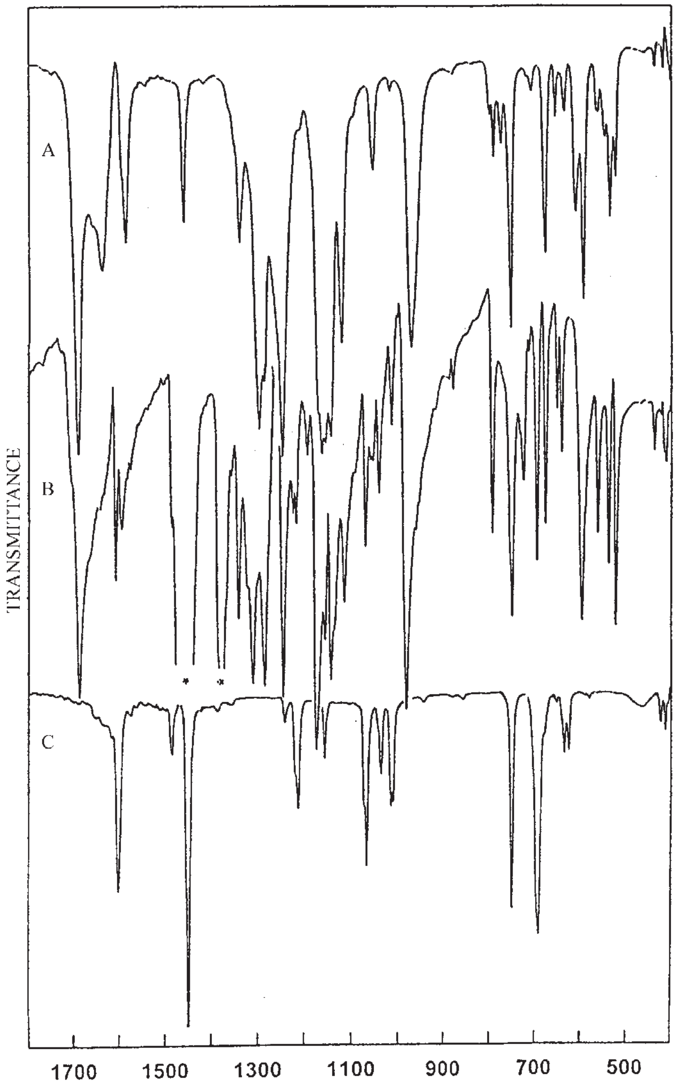

Figure 2. LNT FT infrared spectra of HgCl(sac) (A), [HgCl(py)(sac)]$_2$ (B) and Hg(py)$_2$Cl$_2$ (C) in the 1800–400 cm^{-1} region (the asterisks denote Nujol bands).

expected.[7,27,28] Moreover, in the case of pyridine adducts, several bands from the internal modes of the pyridine ring are also expected in the 1375–1130 cm^{-1} region.[29] The benzenoid stretching bands, however, are found to be sharper and less intense than those arising from the sulphonyl stretches and thus the strongest bands in the mentioned spectral region are usually

TABLE V

Values of C–O and S–O distances and O–S–O angles as well as the frequencies of the CO and SO_2 stretching vibrations in $[HgCl)(py)(sac)]_2$ and HgCl(sac)

Data	Compound	
	$[HgCl(py)(sac)]_2$	HgCl(sac)
d(C–O) / Å	1.204	1.23
d(S–O) / Å	1.439; 1.416	1.426; 1.433
∠(O–S–O) / °	115.8	117.2
$\tilde{\nu}[\nu(CO)]$ / cm^{-1}	1686	1694
$\tilde{\nu}[\nu_{as}(SO_2)]$ / cm^{-1}	1310	1300
$\tilde{\nu}[\nu_{s}(SO_2)]$ / cm^{-1}	1174	1163
$\{\tilde{\nu}[\nu_{as}(SO_2)] - \tilde{\nu}[\nu_{s}(SO_2)]\}$ / cm^{-1}	136	137

attributed to the antisymmetric and symmetric $\nu(SO_2)$ modes. The fact that $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ frequencies in the spectra of different saccharinates are considerably influenced by the values of the O–S–O angles in the respective structure[34] should be considered as well.

Having all this in mind, it might be expected that the similarity of the S–O distances and the O–S–O angle in the structures of HgCl(sac) and $[HgCl(py)(sac)]_2$ (Table V) will lead to the similarity between the SO_2 stretching frequencies in their infrared spectra. As seen from Figure 2 and Table V, the frequency of the symmetric SO_2 stretching mode in the infrared spectrum of HgCl(sac) (1163 cm^{-1}) is close to that belonging to the corresponding mode in $[HgCl(py)(sac)]_2$ (1174 cm^{-1}). The assignment of the band originating from the antisymmetric SO_2 stretching vibration, however, is not straightforward. Namely, two strong bands appear in the $\nu_{as}(SO_2)$ region. The above discussed structural similarity between the SO_2 groups in HgCl(sac) and $[HgCl(py)(sac)]_2$ as well as the comparison of their infrared spectra (Figure 2) enables attributing the band at 1310 cm^{-1} to the antisymmetric SO_2 stretching vibration.

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REFERENCES

1. O. V. Quinzani, S. Tarulli, O. E. Piro. E. J. Baran, and E. E. Castellano, *Z. Naturforsch. B: Chem. Sci.* **52** (1997) 183–187.
2. Jianmin Li, Jingzhen Sun, Pengcheng Chen, and Xintao Wu, *Cryst. Res. Technol.* **30** (1995) 353–358.
3. Jianmin Li, Yanxiong Ke, Quanming Wang, and Xintao Wu, *Cryst. Res. Technol.* **32** (1997) 481–483.
4. Jianmin Li, Huidong Chen, Quingjin Wu, and Xintao Wu, *Cryst. Res. Technol.* **28** (1993) 181–186.
5. A. Hergold-Brundić, B. Kamenar, and G. Jovanovski, *Acta Crystallogr., Sect. C* **45** (1989) 556–558.
6. A. Hergold-Brundić, O. Grupče, and G. Jovanovski, *Acta Crystallogr., Sect. C* **47** (1991) 2659–2660.
7. O. Grupče, G. Jovanovski, and V. Mirčeski, *Spectrosc. Lett.* **27** (1994) 691–699.
8. O. Grupče, G. Jovanovski, and V. Mirčeski, *Bull. Chem. Technol. Macedonia* **15** (1996) 87–92.
9. W. R. Busing and H. A. Levy, *Acta Crystallogr.* **10** (1957) 180–182.
10. A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect A* **24** (1968) 351–359.
11. N. Walker and D. Stuart, *Acta Crystallogr., Sect. A* **39** (1983) 158–166.
12. A. L. Spek, PLATON. Program for the Automated Analysis of Molecular Geometry. Version of February 1996, University of Utrecht, The Netherlands.
13. Th. Hahn (Ed.), *International Tables for X-ray Crystallography*. Vol. A. *Space-group symmetry,* D. Reidel Publishing Company, Dordrecht, 1984.
14. Stoe & Cie (1995a) STADI4. Diffractometer Control Program, Version 1.05b, Stoe & Cie, Darmstadt, Germany.
15. Stoe & Cie (1995b) X-RED. Data Reduction Program, Version 1.05b, Stoe & Cie, Darmstadt, Germany.
16. Stoe & Cie (1995c) EMPIR. Program for Empirical Absorption Correction, Version 1.05b, Stoe & Cie, Darmstadt, Germany.
17. E. J. Gabe, Y. Le. Page, J-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Crystallogr.* **22** (1989) 384–387.
18. G. M. Sheldrick, SHELXL97. Release 97-1. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
19. M. N. Burnett and C. K. Johnson, ORTEP-III. Report ORNL–6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA, 1996.
20. T. Steiner and W. Saenger, *J. Am. Chem. Soc.* **115** (1993) 4540–4547.
21. S. Kasselouri, A. Garoufis, S. Paschalidou, S. P. Perlepes, I. S. Butler, and N. Hadjiliadis, *Inorg. Chim. Acta* **227** (1994) 129–136.
22. P. L. Goggin, P. King, D. M. McEwan, G. E. Taylor, P. Woodward, and M. Sandström, *J. Chem. Soc., Dalton Trans*. (1982) 875–882.
23. C.–W. Chan, S.-M. Peng, and C.-M. Che, *Inorg. Chem.* **33** (1994) 3656–3659.
24. G. Jovanovski, B. Kamenar, G. Ferguson, and B. Kaitner, *Acta Crystallogr., Sect. C* **44** (1988) 616–618.
25. B. Kamenar, G. Jovanovski, and D. Grdenić, *Cryst. Struct. Commun.* **11** (1982) 263–268.
26. D. Grdenić, *Q. Rev. Chem. Soc.* **19** (1965) 303–328.
27. I. Hase, *J. Mol. Struct.* **48** (1978) 33–42.

28. I. Hase, *J. Mol. Struct.* **52** (1979) 163–173.
29. A. Draeger, *Spectrochim. Acta* **39A** (1983) 809–825.
30. G. Jovanovski, B. Šoptrajanov, and *J. Mol. Struct.* **174** (1988) 467–472.
31. G. Jovanovski, B. Šoptrajanov, and B. Kamenar, *Bull. Chem. Technol. Macedonia*, **8** (1990) 47–66.
32. W. R. Feairheller and J. E. Katon, *Spectrochim. Acta* **20** (1964) 1099–1108.
33. T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta* **27A** (1971) 107–118.
34. G. Jovanovski, S. Tančeva, and B. Šoptrajanov, *Spectrosc. Lett.* **28** (1995) 1095–1109.
35. I. G. Binev, B. A. Stamboliyska, and E. A. Velcheva, *Spectrochim. Acta* **52A** (1996) 1135–1143.

SAŽETAK

Strukturna istraživanja di-μ-kloro-bis[saharinatopiridinžive(II)] metodama rentgenske difrakcije i FT IR spektroskopije

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Određena je kristalna i molekulska struktura di-μ-kloro-bis[saharinatopiridinžive(II)]. Istraživanjem FT IR spektra naslovnog spoja u području vibracija CO i SO_2 prepoznate su odgovarajuće vrpce te su im pripisane svojstvene istezne vibracije. Dvije monomerne jedinke klorosaharinatopiridinžive(II) povezane su simetrijskom operacijom centra inverzije, stvarajući na taj način di-μ-kloro premošteni dimer. Atom žive koordiniran je s dva premosna atoma klora i dušikovim atomima piridina i saharinatnog liganda u obliku vrlo nepravilnog tetraedra. Duljine veza živa–klor međusobno se znatno razlikuju i iznose 2,533(2) i 2,715(2) Å, što je ustanovljeno i za vrijednosti duljina valentnih veza živa–dušik koje su 2,106(7) and 2,209(7) Å. Nepravilnost tetraedarske koordinacije žive očituje se u velikom odstupanju od mjerodavne vrijednosti tetraedarskog kuta s malim kutom Cl1–Hg1–$Cl1^i$ [86,23(7)°] i razmjerno vrlo velikim kutom N11–Hg1–N21 [131,5(3)°]. Struktura je izgrađena od izdvojenih molekula povezanih međusobno slabim elektrostatskim privlačenjima vrste C–H···O kraćima od 3,5 Å.