



A new acesulfamato complex: [Cu(acesulfamato)₂(H₂O)₄]. Structural and spectroscopic characterization

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ABSTRACT

The crystal structure of tetraaqua-bis(6-methyl-1,2,3-oxathiazin-4(3H)-onato 2,2-dioxide) copper(II) complex, for short [Cu(ace)₂(H₂O)₄], was determined by X-ray diffraction methods. The complex crystallizes in the monoclinic C2/c space group with a = 11.9838(4), b = 9.5240(3), c = 15.1686(6) Å, β = 102.975(4)° and Z = 4 molecules per unit cell. The structure was determined from 1609 reflections with I > 2σ(I) and refined to an agreement R1-factor of 0.0345. [Cu(ace)₂(H₂O)₄] is a new member in the family of acesulfamate complexes of first row transition metals, namely [M(ace)₂(H₂O)₄], M: Co, Ni, Zn. It differs from the other members in the bonding of acesulfamate to metal through one of its sulfoxide oxygen atoms. The new complex was further characterized by its infrared, Raman and electronic absorption spectra, which were discussed in comparison with those of other related species.

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1. Introduction

Acesulfame-K, the potassium salt of 6-methyl-1,2,3-oxathiazin-4(3H)-one-2,2-dioxide, is one of the most widely used low-calorie artificial sweeteners [1,2] and its general chemical and biological properties have been thoroughly investigated [3,4].

From the chemical and structural points of view, the acesulfamate anion bears some resemblance to saccharin (1,2-benzothiazole-3(2H)-one-1,1-dioxide, see Fig. 1), whose coordination capacity has been intensively exploited during the last years (for a recent review cf. [5]). Similarly to saccharinate, the acesulfamate anion presents different potential coordination sites (the imine nitrogen, the carbonyl oxygen and the two sulfonyl oxygen atoms) and it can act as a mono-dentate, bi-dentate or bridging ligand. This versatility has been widely exploited and numerous metal complexes containing the acesulfamate ligand have been reported and characterized during the last years (cf. for example [6] and references therein). On the other hand, and aside of the structure of the potassium salt, known for more than forty years [7], other simple salts of this anion have been prepared and

characterized only in recent years [8–14].

Acesulfamate complexes of first row transition metals with chemical formula [M(ace)₂(H₂O)₄], M: Co, Ni, Zn are, except for the metal identity, isomers to one another. They only differ in the acesulfamate binding-to-metal mode. In all these complexes, the metal is in an elongated octahedral environment, equatorially coordinated to four water molecules and axially to two ace ligands. In the cobalt complex ace binds to the metal through its N-atom [15] while in the isomorphous [M(ace)₂(H₂O)₄], M: Ni, Zn complexes, through the carbonyl O-atom [16,17]. As a contribution to the crystal chemistry of acesulfamate complexes of transition metals and also as a further study on the chelating ability of the acesulfamate ligand, we report here the crystal structure of yet another member of the series, namely [Cu(ace)₂(H₂O)₄], where ace binds the metal through one of its sulfoxide O-atoms.

2. Experimental

2.1. Materials and physical measurements

Potassium acesulfamate was supplied by Fluka (Sigma-Aldrich, Steinheim, Germany), basic copper(II) carbonate was from Mallinckrodt (Mallinckrodt Chemical Corp., St. Louis, USA) and all the

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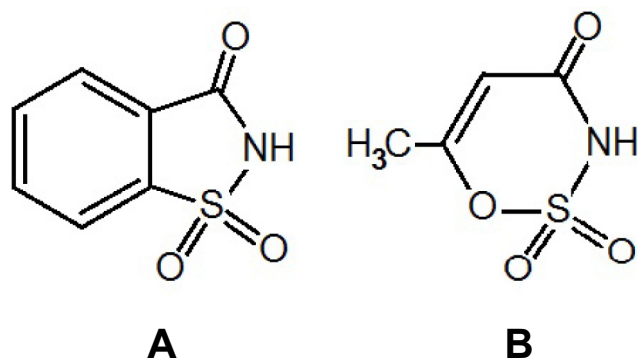


Fig. 1. Schematic drawings of the structures of saccharin (A) and acesulfamic acid (B).

other employed reagents were from Merck (Darmstadt, Germany), analytical grade, and were used as purchased. Elemental analysis was performed with a Carlo Erba (Milano, Italy) model EA 1108 elemental analyzer.

The infrared absorption spectra were recorded on a FTIR-Bruker-EQUINOX 55 spectrophotometer (Bruker Optics Inc., Billerica, MA, USA), in the spectral frequency range between 4000 and 400 cm^{-1} , using the KBr pellet technique. Raman spectra were obtained in the same spectral range with a Thermo Scientific DXR Raman microscope (Thermo Fisher Scientific, Waltham, MA, USA), using the 532 nm line of a Thermo-Scientific solid state laser diode pump for excitation. Electronic absorption spectra were measured on aqueous solutions of the complex, with a Shimadzu (Shimadzu Corporation, Durham, NC, USA) model UV-300 spectrophotometer, using 10-mm quartz cells.

2.2. Synthesis of the complex

Acesulfamic acid was prepared as described by Velaga et al. [18], as follows: To 5.00 g of potassium acesulfamate dissolved in a small portion of water (ca. 10 mL), 6 mL of concentrated HCl was added drop-wise. The generated acid was extracted with 20 mL of ethyl acetate. After evaporation of the solvent in air a colorless solid was deposited. It was re-crystallized twice from ethyl acetate, generating a deposit of needle-like colorless crystals, after slow evaporation of the solvent in air (m. p. 122–124 $^{\circ}\text{C}$ [18]).

For the synthesis of the Cu(II) complex, 4.0 mmol of acesulfamic acid was dissolved in 15 mL of distilled water and heated to 75 $^{\circ}\text{C}$. To this solution, 1.2 mmol (slight excess) of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ was slowly added, under constant stirring. After this addition, the solution was stirred for another 30 min at the same temperature. The remaining, not reacted copper carbonate was separated by filtration and finally the resulting solution was left to evaporate in air. After a few days a blue colored powder, highly soluble in water, was collected and re-crystallized from water with a yield of ca. 95%. The purity of the compound was confirmed by elemental analysis: Calc. for $\text{C}_8\text{H}_{16}\text{CuN}_2\text{O}_{12}\text{S}_2$ (459.89): C 20.89, H 3.48, N 6.09, S 13.94%. Found: C 20.80, H 3.52, N 6.05, S 13.90%. Single crystals adequate for X-ray diffraction studies were selected from the crystalline mass employing a microscope.

2.3. X-ray crystallography and structure solution

The measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation. X-ray diffraction intensities were collected (ω scans with θ and κ -offsets), integrated and scaled with CrysAlisPro [19] suite of programs. The unit cell parameters were

obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro.

The structure was solved by intrinsic phasing with SHELXT [20] and refined by least-squares with SHELXL [21].

The acesulfamate hydrogen atoms were positioned on stereochemical basis and refined with the riding model. The methyl hydrogen atoms locations were optimized during the refinement by treating them as rigid bodies which were allowed to rotate around the corresponding C–CH $_3$ bond such as maximize the sum of the residual electron density at their calculated positions. As a result, the methyl groups converged to staggered angular conformations. The waters H-atoms were located in a difference Fourier map and refined at their found position with isotropic displacement parameters and Ow–H and H \cdots H distances restrained to target values of 0.86(1) and 1.36(1) Å, respectively. Crystal data and refinement results are summarized in Table 1.

Complete crystallographic data for $[\text{Cu}(\text{acesulfamato})_2(\text{H}_2\text{O})_4]$ has been deposited with the Cambridge Crystallographic Data Centre, CCDC 1953538. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Description of the structure

An ORTEP [22] plot of the copper acesulfamate complex is shown in Fig. 2. Bond distances within the acesulfamate molecule are detailed in Table 2 and short contact distances around the metal are listed in Table 3.

The observed bond distances and angles within the acesulfamate anion are in general agreement with corresponding values reported for other members of the $\text{M}(\text{ace})_2(\text{H}_2\text{O})_4$, M: Co, Ni, Zn family of transition metal complexes [15–17], other divalent metal salt, namely $\text{Ca}(\text{ace})_2$ [8], $\text{Cd}(\text{ace})_2(\text{H}_2\text{O})_2$ and $\text{Pb}(\text{ace})_2$ [23] and also for the ammonium salt [9], $\text{Li}(\text{ace})\text{H}_2\text{O}$ [14] and the M-ace (M: Na, K, Rb, Cs) isomorphous series of alkaline metal salts [7,10]. Particularly, the short C3–C4 distances of 1.318(4) Å confirms the formal double bond character expected for this link. The carbonyl $>\text{C}=\text{O}$ double bond distance is 1.251(3) Å and sulfoxide $\text{S}=\text{O}$ distances are 1.414(2) and 1.415(3) Å. The other ring single bond lengths are $d(\text{C}-\text{O}) = 1.385(3)$ Å, $d(\text{O}-\text{S}) = 1.604(2)$ Å, $d(\text{S}-\text{N}) = 1.576(2)$ Å, $d(\text{C}-\text{N}) = 1.344(3)$ Å, and $d(\text{C}-\text{C}) = 1.450(3)$ Å. These bond lengths can be compared with the neutral acesulfamic acid molecule [18]. Major change in the bonding structure of acesulfamate ion occurs at the S–N bond, which upon deprotonation suffers an average shortening of about 0.053 Å (about 19 times the standard error σ). A smaller shortening (-0.038 Å = -10σ) is observed in the N–C bond length. Other major bond length changes when going from neutral acesulfamate to acesulfamate anion are observed for the ring S–O and O–C bonds ($+0.011$ Å = $+5\sigma$ and -0.020 Å = -7σ , respectively).

The complex is sited on a crystallographic two-fold axis with the metal at the center of a square bipyramidal environment (CuO_6 core), equatorially coordinated at the bipyramide basis to four water molecules [$\text{Cu}-\text{Ow}$ bond distances of 1.908(2), 1.962(3) and 1.962(3) Å], two of them (O2w and O3w) laying on the molecular two-fold axis (see Fig. 2). The bipyramide apexes are occupied by one sulfoxide oxygen of two symmetry related ace molecules [$d(\text{Cu}-\text{O}) = 2.484(2)$ Å]. The coordination and metrics around copper(II) ion indicates a $d(x^2-y^2)$ ground state orbital for the unpaired electron (hole).

The crystal is further stabilized by a three-dimensional network

Table 1
Crystal data and structure refinement results for [Cu(ace)₂(H₂O)₄].

| Empirical formula | C ₈ H ₁₆ CuN ₂ O ₁₂ S ₂ |
|--|--|
| Formula weight | 459.89 |
| Temperature (K) | 297(2) |
| Wavelength (Å) | 0.71073 |
| Crystal size (mm ³) | 0.450 × 0.348 × 0.140 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a (Å) | 11.9838(4) |
| b (Å) | 9.5240(3) |
| c (Å) | 15.1686(6) |
| β (°) | 102.975(4) |
| V (Å ³) | 1687.1(1) |
| Z | 4 |
| ρ _{calc.} (g.cm ⁻³) | 1.811 |
| Absorption coefficient (mm ⁻¹) | 1.606 |
| F(000) | 940 |
| θ(°)-range for data collection | 2.905 to 28.958 |
| Index ranges | -10 ≤ h ≤ 15, -7 ≤ k ≤ 12, -18 ≤ l ≤ 20 |
| Reflections collected | 3651 |
| Independent reflections | 1857 [R(int) = 0.022] |
| Observed reflections [I > 2σ(I)] | 1609 |
| Completeness to θ = 25.242° | 99.9% |
| Refinement method | Full-matrix least-squares on F ² |
| Data/restraints/parameters | 1857/4/132 |
| Goodness of fit on F ² | 1.080 |
| R1/wR2 [I > 2σ(I)] | 0.0345/0.0877 |
| R1/wR2 (all data) | 0.0408/0.0941 |
| Largest differ. peak and hole (e.Å ⁻³) | 0.374 and -0.671 |

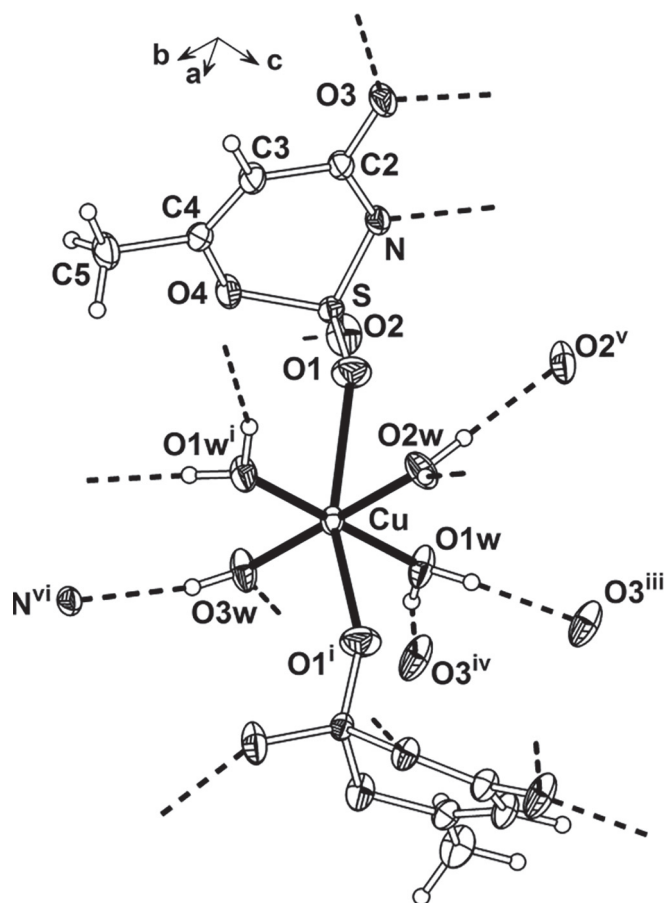


Fig. 2. View of Cu(ace)₂(H₂O)₄ showing the labeling of the non-H atoms and their displacement ellipsoids at the 30% probability level. Copper-ligand bonds are indicated by full lines and H-bonds by dashed lines. Copper(II) and water O2w and O3w oxygen atoms are on a crystallographic two-fold axis. Symmetry operations: (i) -x+1, y, -z+3/2; (#3) x+1/2, -y+1/2, z+1/2; (#4) -x+1/2, y+1/2, -z+3/2; (#5) -x+1/2, y-1/2, -z+3/2; (#6) x+1/2, y+1/2, z.

Table 2
Bond lengths (Å) and angles (°) of the acesulfamate ligand in [Cu(ace)₂(H₂O)₄].

| | | | |
|-------------|----------|----------------|----------|
| C(2)–O(3) | 1.251(3) | N–C(2)–C(3) | 121.0(2) |
| C(2)–N | 1.344(3) | C(4)–C(3)–C(2) | 123.0(2) |
| C(2)–C(3) | 1.450(3) | C(3)–C(4)–O(4) | 120.4(2) |
| C(3)–C(4) | 1.318(4) | C(3)–C(4)–C(5) | 127.8(3) |
| C(4)–O(4) | 1.385(3) | O(4)–C(4)–C(5) | 111.6(2) |
| C(4)–C(5) | 1.485(4) | C(2)–N–S | 118.7(2) |
| N–S | 1.576(2) | C(4)–O(4)–S | 117.7(2) |
| O(1)–S | 1.414(2) | O(1)–S–O(2) | 116.2(1) |
| O(2)–S | 1.415(2) | O(1)–S–N | 111.3(1) |
| O(4)–S | 1.604(2) | O(2)–S–N | 110.8(1) |
| | | O(1)–S–O(4) | 106.9(1) |
| O(3)–C(2)–N | 119.1(2) | O(2)–S–O(4) | 104.3(1) |

Table 3
Short contacts and angles around Cu(II) in [Cu(ace)₂(H₂O)₄].

| | | | |
|----------|----------|-----------------|-----------|
| O(1W)–Cu | 1.908(2) | O(1W)–Cu–O(2W) | 89.84(6) |
| O(2W)–Cu | 1.962(3) | O(1W)–Cu–O(3W) | 90.16(6) |
| O(3W)–Cu | 1.962(3) | O(1W)#1–Cu–O(1) | 88.10(9) |
| O(1)–Cu | 2.484(2) | O(1W)–Cu–O(1) | 91.83(9) |
| | | O(2W)–Cu–O(1) | 77.95(6) |
| | | O(3W)–Cu–O(1) | 102.05(5) |

O(1W)#1 atom is symmetry related to O(1W) through the two-fold axis rotation: x+1, y, -z+3/2.

of medium to strong OwH...A bonds, where the acceptors (A) are the unbounded-to-metal sulfoxide oxygens [d(O2wH...O2(sulf)) = 1.91(1) Å; ∠(O2w-H-O2(sulf)) = 162(3)°], carbonyl oxygens [O1wH...O3(carb) bond distances of 1.77(2) and 1.86(2) Å; O1w-H-O3(carb) bond angles of 164(4) and 159(3)°], and the N-atom [d(O3wH...N) = 2.02(1) Å; ∠(O3w-H-N) = 168(4)°] of neighboring acesulfamate anions. The H-bonding structure is shown in Fig. 2 and further detailed in Table 4.

3.2. Electronic absorption spectrum

The electronic absorption spectrum of the complex

presents a very strong absorption band at 225 nm ($\epsilon = 20.4 \times 10^3 \text{ L.Mol}^{-1}.\text{cm}^{-1}$) and a weaker and relatively broad one, centered at about 800 nm ($\epsilon = 12 \text{ L.Mol}^{-1}.\text{cm}^{-1}$).

The strong high-energy band is, evidently, an internal ligand charge transfer, as in potassium acesulfamate it is found at the same

Table 4
Hydrogen bond distances [Å] and angles [°] for $[\text{Cu}(\text{ace})_2(\text{H}_2\text{O})_4]$.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{D-H}\cdots\text{A})$ |
|----------------------|---------|----------|----------|------------------------------------|
| C(5)-H(5A)...O(2)#2 | 0.96 | 2.51 | 3.426(4) | 160.3 |
| O(1W)-H(1A)...O(3)#3 | 0.85(1) | 1.86(2) | 2.670(3) | 159(3) |
| O(1W)-H(1B)...O(3)#4 | 0.85(1) | 1.77(2) | 2.598(3) | 164(4) |
| O(2W)-H(2A)...O(2)#5 | 0.85(1) | 1.91(1) | 2.733(3) | 162(3) |
| O(3W)-H(3A)...N#6 | 0.85(1) | 2.02(1) | 2.861(2) | 168(4) |

Symmetry transformations: (#2) $x, -y+1, z-1/2$; (#3) $x+1/2, -y+1/2, z+1/2$; (#4) $-x+1/2, y+1/2, -z+3/2$; (#5) $-x+1/2, y-1/2, -z+3/2$; (#6) $x+1/2, y+1/2, z$.

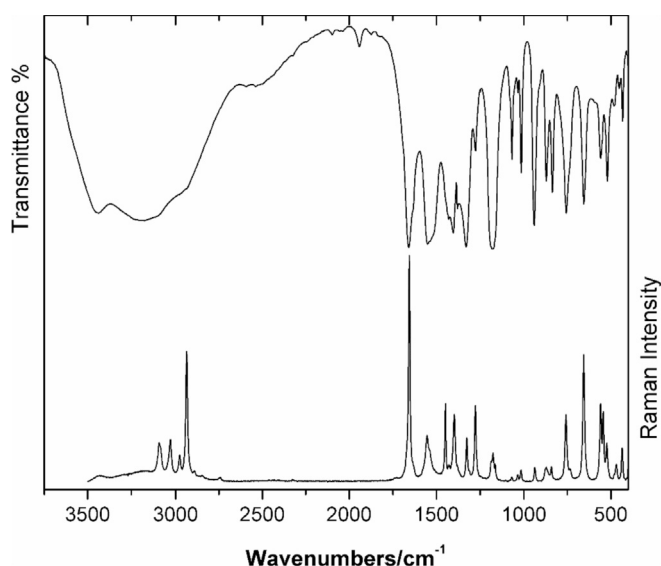


Fig. 3. FTIR spectrum (above) and FT-Raman spectrum (below) from $[\text{Cu}(\text{ace})_2(\text{H}_2\text{O})_4]$ in the spectral range between 4000 and 400 cm^{-1} .

energy [24–26]. This transition is probably a $\pi \rightarrow \pi^*$ charge transfer, similar as that found in phthalimide (1H-isoindole-1,3(2H)-dione) and in benzoates and benzamides [27]. The second, weak and relatively broad band is the typical ${}^2E_g \rightarrow {}^2T_{2g}$ transition expected for a distorted octahedral Cu(II) complex [28,29]. This spectroscopic result is consistent with the presence of a tetragonally distorted Cu(II) complex with four short metal-ligand bonds (Cu–OH₂ in this case) in one plane and two longer metal-ligand bonds (Cu–OSO, in this case) along the axis perpendicular to that plane (cf. again Fig. 2) [29].

3.3. Vibrational spectra

The FTIR and FT-Raman spectra of the complex are shown in Fig. 3 and the proposed assignments are presented in Table 5. These assignments were performed on the basis of a recent experimental and DFT-theoretical study of potassium acesulfamate [30], additionally supported by our previous studies [9–11,13,14,22], and is briefly discussed in the following.

–The O–H stretching vibrations of the water molecules generate a relatively strong and broad IR-band and, as it is usual, they are only seen as two weak signals in the Raman spectrum. The corresponding deformational modes, $\delta(\text{H}_2\text{O})$, are probably overlapped with the strong bands found in the 1550–1660 cm^{-1} region. The weak IR-band found at 452 cm^{-1} (468 cm^{-1} in the Raman spectrum) was tentatively assigned to a $\rho_w(\text{H}_2\text{O})$ wagging mode.

–Bands related to the CH and CH₃ stretching modes could be clearly identified in the Raman spectrum and are very weak in the IR-spectrum in which some of them appear partially superimposed with the broad H₂O stretching.

–As in the previously investigated cases, vibration modes related to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{C})$ stretching vibrations are strongly coupled and result in two of the most intense IR bands. Both IR bands show split signals, whereas in the Raman spectrum only the lower energy band presents a shoulder on its lower-energy side.

–Bands related to the vibrational modes of the sulfonyl moiety appear in the usual range although, interestingly, the $\nu_{\text{as}}(\text{SO}_2)$ stretching vibration is partially split and located at a somewhat lower energy than in the previously investigated cases. Both

Table 5
Assignment of the FTIR and FT-Raman spectrum of $[\text{Cu}(\text{ace})_2(\text{H}_2\text{O})_4]$ (band positions in cm^{-1}).

| Infrared | Raman | Assignments |
|------------------------------------|-------------------------|---|
| 3483 w, 3173vs, br | 3430 vw, 3190 vw, br | $\nu(\text{O}-\text{H}) (\text{H}_2\text{O})$ |
| 3085 sh | 3093 m, 3028 m | $\nu(\text{CH})$ |
| | 2976 w | $\nu_{\text{as}}(\text{CH}_3)$ |
| 2935 sh | 2935 vs | $\nu_{\text{s}}(\text{CH}_3)$ |
| 2090 vw, 1942 w, 1873 vw | | Combinations or overtones |
| 1658 vs, 1634 sh, 1550 vs, 1516 sh | 1655 vs, 1553m/1510sh | $\nu(\text{C}=\text{O}) + \nu(\text{C}-\text{C})_{\text{ring}}$ |
| 1429 w, 1403 s | 1447 m, 1427 vw, 1396 m | $\delta(\text{CH}_3)$ |
| 1378 w, 1328 vs | 1325 m | $\nu_{\text{as}}(\text{SO}_2)$ |
| 1274 m | 1275 m | $\nu(\text{CN}) + \nu(\text{OC}) + \delta(\text{CCH})$ |
| 1180 vs | 1177 w, 1165 m | $\nu_{\text{s}}(\text{SO}_2) + \nu(\text{SN})$ |
| 1068 s | 1070 vw | $\delta(\text{CH}_3)$ |
| 1034 w, 1016 m | 1036 vw, 1017 w | $\nu(\text{C}-\text{C}) + \nu(\text{SN})$ |
| 940 vs | 937 w | $\nu(\text{OC}) + \nu(\text{C}-\text{CH}_3)$ |
| 872 m | 871 w | τ_{ring} |
| 836 s | 842 w | $\nu(\text{SN}) + \nu(\text{C}-\text{C}) + \delta(\text{NCO})$ |
| 757 s, 738 sh | 758 m, 734 vw | τ_{ring} |
| 655 s | 656 s | δ_{ring} |
| 558 m, 520 s | 559 m, 543 m | $\delta_{\text{ring}} + \delta(\text{SO}_2)$ |
| 482 w | 523 w | τ_{ring} |
| 452 w | 468 w | $\rho_w(\text{H}_2\text{O})$ |
| 432 m | 435 m | δ_{ring} |

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; br: broad; sh: shoulder.

effects can probably be related to the bonding of this moiety to the metal center. Similar effects cannot be observed in the corresponding $\nu_s(\text{SO}_2)$ mode, because this vibration is strongly coupled with other vibrational modes [30].

Authorship statement

All the authors agrees with the presentation of this paper in its present form. All of the authors have participated actively in the development of this research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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