Palladium(II) and Platinum(II) Complexes of N-3-Pyridinylmethanesulfonamide

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IR Spectra, Palladium(II) and Platinum(II) Complexes, N-3-Pyridinylmethanesulfonamide

The complexes cis-[Pd(PMSA)2Cl2], cis-[Pt(PMSA)2X2], trans-[Pt(PMSA)2I2] and [Pt(PMSA)4]Cl2 (PMSA = N-3-pyridinylmethanesulfonamide; X = Cl, Br, I) have been synthesized and characterized by elemental analysis, molar electric conductivity, IR and 1H NMR spectra. A detailed assignment of the IR spectra (4000-150 cm⁻¹) of the complexes, supported by an approximate normal coordinate analysis, has been performed. The complexes are of square-planar type and the PMSA ligand is coordinated via the pyridine nitrogen atom.

Introduction

The search for novel metal-based carcinostatics with improved therapeutic characteristics with respect to the parent compound cisplatin [1] remains a topical problem of biocoordination chemistry. Methanesulfonamide derivatives possess DNA-binding ability, show cytostatic effects, and some of them, like Amscarine, find application in cancer chemotherapy [2–5]. Having hydrophilic character, the sulfonyl group is considered as a suitable pharmacophoric equivalent for replacing functional groups in drug design [6]. Recently we studied the conformational and spectroscopic features [7–9], as well as the biological activity [8] of methylsulfonylhydrazine and its azomethine derivatives. Mesylated aminopyridines and their platinum complexes could also be of interest from the view point of experimental cancer chemotherapy. There is an increasing interest in platinum complexes with pyridine-type ligands due to the unexpectedly high cytotoxic activity of such complexes having trans-configuration of the N-donor ligands. [10, 11]. Recently we published [12] a vibrational spectroscopic study of N-3-pyridinylmethanesulfonamide (PMSA), but the coordination chemistry of this potential ligand has not been explored.

The subject of present work is the preparation and spectroscopic characterization of a series of coordination compounds of PMSA (Fig. 1) with palladium(II) and platinum(II).

Results and Discussion

For the synthesis of the new complexes, standard methods [13] based on the difference in the trans-effect of halide and nitrogen-donor ligands were applied. Attempts to prepare the corresponding thiocyanato complex, cis-[Pt(PMSA)2(SCN)2], by combining aqueous solutions of PMSA and K2[Pt(SCN)4], were also undertaken. The product obtained gave a satisfactory elemental analysis in agreement with the above stoichiometry, but the 1H NMR spectrum revealed the presence of several components. The trials to obtain a single product remained unsuccessful.

In Table 1 the formulae, analytical results and some physical properties of the complexes prepared are listed. All the complexes, except 6 are soluble in dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) and acetone. The cis-complexes are soluble in nitromethane as distinct from the trans-complex 5. Complexes 2 and 6 are soluble in hot water. Compounds 2 and 3 can be
recrystallized from water and nitromethane, respectively, although this is not necessary for obtaining analytically pure products. Compound 6 gives precipitates with tetrachloroplatinate(II) and with oxalate anions; they are pale cream and white, respectively.

The molar electric conductivity \( (A_m) \) values (Table 1) for the dihalo complexes measured in acetone are typical for nonelectrolytes [14], which indicates their non-ionic character. However, the \( A_m \) value for the aqueous solution of 6 is characteristic for the 2:1 electrolyte type [15], which shows that the compound consists of \([Pt(PMSA)_4]^{2+}\) cations and chloride anions.

**Infrared (IR) spectra**

**Ligand vibrations.** A full interpretation of the IR spectrum of PMSA in the range of 4000–150 cm\(^{-1}\), supported by \textit{ab initio} vibrational analysis, has recently been published by us [12]. Data for the fundamental vibrations of PMSA in the free state and in the new complexes are collected in Table 2. These assignments are based on the literature data for molecules containing similar fragments – pyridine(s) [16–21], and methanesulfonamide derivatives [7–9, 22–25] (an expanded reference list can be found in [12]), as well as for coordinated pyridines [26–29]. The two lowest frequency modes, the torsions around the SN and CN bonds fall outside the range of the spectrometer used. For the notations of the vibrational modes of the pyridine fragment of PMSA, we have accepted the scheme based on the correlation between the pyridine and benzene vibrations according to Wilson [18].

In the solid-state spectrum of free PMSA, the NH stretching appears as a broad band at quite a low frequency, 2860–2709 cm\(^{-1}\), and this has been explained [12] by the presence of strong intermolecular hydrogen bonds involving the pyridine nitrogen atom and the hydrogen atom of the SO\(_2\)NH group. Upon coordination of the pyridine nitrogen atom of PMSA to a metal, it loses the ability to participate in hydrogen-bonding, and an increase in the frequency of the NH stretching vibration is to be expected. As seen from Table 2, the corresponding frequency indeed increases: by ca. 470 cm\(^{-1}\) for the non-ionic complexes 1–5, and by ca. 250 cm\(^{-1}\) for the cationic complex 6. Thus, the suggestion that the low-frequency shift of the NH stretching band of PMSA is due to hydrogen-bonding finds an additional support. The assignment of the \( v(\text{NH}) \) band of 6 was confirmed by deuteration: in the spectrum of the deuterated sample a new band centred at 2295 cm\(^{-1}\) appears \((v_H/v_D\) isotopic ratio of 1.32). The less pronounced increase in the NH stretching frequency for 6 can be explained by hydrogen bonding of the type NH...Cl\(^-\) involving the sulfonamide hydrogen atom of the complex cation \([Pt(PMSA)_4]^{2+}\).
Table 2. IR spectroscopic data for PMSA and its complexes: wave numbers (\(\nu\) [cm\(^{-1}\)]) of the fundamental vibrations of the free and coordinated ligand.

<table>
<thead>
<tr>
<th>Compound No</th>
<th>Assignment (\nu) (PMSA)</th>
<th>Assignment (\nu) (Py)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1301 m (\nu(CH_2))</td>
<td>(\nu(CH_2))</td>
</tr>
<tr>
<td>2</td>
<td>1313 m (\nu(CH_2))</td>
<td>(\nu(CH_2))</td>
</tr>
<tr>
<td>3</td>
<td>1150 s (\nu(SO_2))</td>
<td>(\nu(SO_2))</td>
</tr>
<tr>
<td>4</td>
<td>1334 s (\nu(SO_2))</td>
<td>(\nu(SO_2))</td>
</tr>
<tr>
<td>5</td>
<td>1193 w (\nu(CH_2))</td>
<td>(\nu(CH_2))</td>
</tr>
<tr>
<td>6</td>
<td>1313 m (\nu(CH_2))</td>
<td>(\nu(CH_2))</td>
</tr>
</tbody>
</table>

Assignments:
- \(\nu(CH_2)\): C\(_2\)-hydride stretching vibration
- \(\nu(SO_2)\): S=O stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
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- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
- \(\nu(CH_2)\): \(\nu(CH_2)\) stretching vibration
Table 2 (continued).

<table>
<thead>
<tr>
<th>PMSA</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Assignmentb</th>
</tr>
</thead>
<tbody>
<tr>
<td>289 w</td>
<td>289 w</td>
<td>292 sh</td>
<td>292 w</td>
<td>285 sh</td>
<td>293 w</td>
<td>282 w</td>
<td>r(SO₂)</td>
</tr>
<tr>
<td>244 w</td>
<td>245 w</td>
<td>246 sh</td>
<td>241 w</td>
<td>247 w</td>
<td>249 w</td>
<td>243 w</td>
<td>t(ring) – py(16b)</td>
</tr>
<tr>
<td>228 w</td>
<td>229 w</td>
<td>228 w</td>
<td>(222)c</td>
<td>230 w</td>
<td>221 w</td>
<td>226 w</td>
<td>t(CS)</td>
</tr>
<tr>
<td>166 w</td>
<td>175 w</td>
<td>171 w</td>
<td>160 w</td>
<td>158 sh</td>
<td>161 w</td>
<td>157 m</td>
<td>δ(CNS)</td>
</tr>
</tbody>
</table>

a Abbreviations: b – broad, c – complex, m – medium, s – strong, sh – shoulder, w – weak; b notations: as – asymmetric, py(i) – pyridine ring vibration with number i, according to Wilson scheme, s – symmetric, t – torsional, δ – in-plane bending, v – stretching, θ – out-of-plane bending, q – rocking, τ – twisting, ω – wagging; c overlapped by the band(s) indicated in brackets.

The coordination also affects the vibrational frequencies of the pyridine fragment. The band shifts observed are in accordance with the regularities found for other complexes of pyridine and its derivatives [26–28, 30].

Vibrations of the coordination node. The assignment of the ligand bands in the far IR region is a prerequisite for the identification of the vibrations of the coordination node. The latter include: a) modes of the coordination tetragon (the skeleton MN₂X₂ or PtN₄), and b) the rocking, wagging and torsional modes of the ligands toward the coordination tetragon. For a more reliable assignment of these low-frequency bands, and especially for identifying the bands of the coordination quadrangle, we undertook a normal coordinate analysis (NCA) for model fragments of the complex molecules. Approximate NCA has been performed by Saito et al. [31] for the complexes [Zn(pyridine)₂X₂] (X = Cl, Br, I) taking into account only the ZnN₂X₂ skeleton, each of the N atoms being considered to have the mass of the complete pyridine ligand.

We have chosen a compromise between the NCA of an entire complex molecule and the approach of Saito et al. Our model is illustrated in Fig. 2. The metal, the donor atoms and their nearest surroundings – the α-carbon atoms of the pyridine rings – were taken into consideration. The carbon atoms were considered to have an effective atomic mass of 25.03 (their own mass plus that of their adjacent C and H atoms). Typical values were ascribed to the bond lengths and bond angles at the metal and nitrogen atoms on the basis of X-ray diffraction data for similar complexes with appropriate ligands [10, 32–42]. The values of the torsional angles about the MN bonds in the model of complexes 1–4 and 5 correspond to those in cis-[Pt(pyridine)₂Cl₂] and trans-[Pt(pyridine)₂Cl₂], respectively [32], whereas in the model of 6 they correspond to an idealized version (C₂h symmetry) of the structure of [Pt(pyridine)₄]Cl₂·3H₂O [34].

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Regarding the torsional angles about the MN bonds, a crystallographic literature survey shows the following regularities: In the square-planar
complexes of the type cis-[ML$_2$X$_2$] (M = Pd, Pt, L = pyridine or pyridine-like aromatic heterocycle; X = Cl, Br, I), the planar L ligands are rotated in the same direction with respect to the coordination plane, at an angle near to 60° to give approximate $C_2$ symmetry [32, 33, 38] (Fig. 2A); in the trans-complexes of the above type, the L ligands are rotated in opposite directions towards the coordination plane to reach roughly $C_{2h}$ symmetry [10, 32, 35, 37, 39] (Fig. 2B); in the complexes with the [ML$_4$]$^2^+$ unit one pair of ligands is rotated in the opposite direction towards the other pair to give approximate $C_{2h}$ symmetry [34, 40, 41a] (Fig. 2C).

The model chosen gives rise to 21 normal vibrations for structures A and B, and 33 for structure C (Fig. 2). Nine of them (7 in-plane and 2 out-of-plane modes) belong to the coordination tetragon (MN$_2$X$_2$ or PtN$_4$), and the remaining are classified as follows: 4(8) CN stretching, 2(4) CNC bending, 2(4) C$_2$NM rocking, 2(4) C$_2$NM wagging and 2(4) torsional around CN bonds (their number for the case C is given in parenthesis).

For all complexes, fixed values were ascribed to the force constants (Table 4) of the CNC fragments, as well as to the CNM in-plane bending force constants. The later were chosen so as the wave numbers for the C$_2$NM rocking modes to fall in the range of 408–361 cm$^{-1}$ because in this range extra bands were observed in the spectra of some complexes (vide infra), which could not be ascribed to ligand vibrations or to vibrations of the coordination tetragon. The force constants of the CNC fragments were chosen so as to reproduce approximately the wave numbers of the pyridine ring vibrations py(8b), py(9a) and py(6a). The out-of-plane vibrations, which fall in the lowest-frequency range, were inaccessible in our experiments, and the corresponding force constants could not be optimized. We have given values for these force constants which produce acceptable wave numbers for the corresponding modes, taking into account the data available for similar complexes [43, 44]. This seems justified since the potential energy distribution showed a lack of significant mixing between the in-plane and out-of-plane motions. Our attention focused on the in-plane vibrations of the coordination tetragon, and for this purpose the model chosen appears to be reasonable.

The far IR spectra of the cis-/trans- isomers 4 and 5 are illustrated in Fig. 3. The assignment of the IR bands (400–150 cm$^{-1}$) of the coordination tetragon for all the studied complexes, compared with the results from the approximate NCA for the corresponding model fragments are collected in Table 3; the force constants that reproduce these results are given in Table 4. The assignments in Table 3 are in good agreement with the literature data for Pd(II) and Pt(II) complexes with similar ligands [27, 29, 37, 43–46]. The bands of the XPtX (X = Br, I) bending modes could not be registered because of instrumental restrictions. For most of the diaminedihalo complexes of Pt(II) and Pd(II), the number of the observed metal-halogen stretching bands corresponds to that predicted by the point group theory, and it is usually considered as indicative concerning the configuration of such complexes [15, 47, 48]. The identification of the metal-halogen stretching bands was facilitated by their relative intensity compared to other low-frequency bands. As expected, two bands of the metal-halogen stretching were observed for the complexes with cis-configuration (1–4), and one band for the trans-complex (5).

The bands of the C$_2$NM rocking modes are difficult to assign since they probably overlap with bands of the $\bar{\delta}$(SO$_2$) and $\bar{\delta}$(CSN) ligand vibrations. The additional bands observed in the spectra of 4 and 5 at 385 cm$^{-1}$, as well as at 381 cm$^{-1}$ in the spectrum of 6, could be ascribed to the $\bar{\delta}$(C$_2$NM) vibrations.
Table 3. Experimental (IR spectra) and calculated (NCA) wave numbers ($v$, cm$^{-1}$) for the fundamental vibrations of structural fragments of PMSA complexes $a, b$ (Fig. 2).

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Structural type, point group</th>
<th>$v_{\text{exptl.}}$</th>
<th>$v_{\text{calcd.}}$</th>
<th>$v_{\text{exptl.}}$</th>
<th>$v_{\text{calcd.}}$</th>
<th>$v_{\text{exptl.}}$</th>
<th>$v_{\text{calcd.}}$</th>
<th>$v_{\text{exptl.}}$</th>
<th>$v_{\text{calcd.}}$</th>
<th>$v_{\text{exptl.}}$</th>
<th>$v_{\text{calcd.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{cis-[M(PMSA)$_2$X$_2$]}, C$_2$(C$_2$V)</td>
<td>361 m</td>
<td>345 m</td>
<td>345 m</td>
<td>325 m</td>
<td>214 m</td>
<td>210 m</td>
<td>169 m</td>
<td>169 m</td>
<td>185 m</td>
<td>197 m</td>
</tr>
<tr>
<td>2</td>
<td>$\text{trans-[Pt(PMSA)$<em>2$I$<em>2$]}, C$</em>{2v}$(D$</em>{2h}$)</td>
<td>340 m</td>
<td>325 m</td>
<td>325 m</td>
<td>280 w</td>
<td>214 m</td>
<td>210 m</td>
<td>169 m</td>
<td>169 m</td>
<td>185 m</td>
<td>222 m</td>
</tr>
<tr>
<td>3</td>
<td>$\text{trans-[Pt(PMSA)$<em>4$Cl$<em>2$]}, C$</em>{2v}$(D$</em>{4h}$)</td>
<td>340 m</td>
<td>325 m</td>
<td>325 m</td>
<td>280 w</td>
<td>214 m</td>
<td>210 m</td>
<td>169 m</td>
<td>169 m</td>
<td>185 m</td>
<td>222 m</td>
</tr>
<tr>
<td>4</td>
<td>$\text{trans-[Pt(PMSA)$<em>4$I$<em>2$]}, C$</em>{2v}$(D$</em>{4h}$)</td>
<td>340 m</td>
<td>325 m</td>
<td>325 m</td>
<td>280 w</td>
<td>214 m</td>
<td>210 m</td>
<td>169 m</td>
<td>169 m</td>
<td>185 m</td>
<td>222 m</td>
</tr>
<tr>
<td>5</td>
<td>$\text{trans-[Pt(PMSA)$<em>4$I$<em>2$]}, C$</em>{2v}$(D$</em>{4h}$)</td>
<td>340 m</td>
<td>325 m</td>
<td>325 m</td>
<td>280 w</td>
<td>214 m</td>
<td>210 m</td>
<td>169 m</td>
<td>169 m</td>
<td>185 m</td>
<td>222 m</td>
</tr>
<tr>
<td>6</td>
<td>$\text{trans-[Pt(PMSA)$<em>4$I$<em>2$]}, C$</em>{2v}$(D$</em>{4h}$)</td>
<td>340 m</td>
<td>325 m</td>
<td>325 m</td>
<td>280 w</td>
<td>214 m</td>
<td>210 m</td>
<td>169 m</td>
<td>169 m</td>
<td>185 m</td>
<td>222 m</td>
</tr>
</tbody>
</table>

$a$ Abbreviations and notations as in Table 2; $b$ the remaining calculated vibrations fall in the ranges: $v$(CN): 1583–1563 and 1304–1244, $d$(CNC): 620–610, $q$(CNM): 408–361, out-of-plane bending (at N and M, respectively) and torsional (around NM bonds): 118–40 cm$^{-1}$; $c$ point group of the entire structural fragment, and of the coordination tetragon per se (in parentheses); $d$ overlapped by the band indicated in brackets; $e$ IR-inactive in the corresponding point group.

Table 4. Force constants $a$ for the structural fragments of PMSA complexes (Fig. 2).

<table>
<thead>
<tr>
<th>Force constant</th>
<th>Compound No</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching [mdyn Å$^{-1}$]</td>
<td>MN</td>
<td>3.16</td>
<td>3.16</td>
<td>2.30</td>
<td>2.22</td>
<td>3.20</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>1.63</td>
<td>1.76</td>
<td>1.89</td>
<td>1.85</td>
<td>1.60</td>
<td></td>
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<tr>
<td>In-plane bending [mdyn Å rad$^{-2}$]</td>
<td>NMM</td>
<td>0.52</td>
<td>0.55</td>
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<td>0.52</td>
<td>0.65</td>
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<tr>
<td></td>
<td>NMX</td>
<td>0.58</td>
<td>0.62</td>
<td>0.61</td>
<td>0.62</td>
<td>0.67</td>
<td></td>
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<tr>
<td></td>
<td>XMX</td>
<td>0.71</td>
<td>0.67</td>
<td>0.67</td>
<td>0.69</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Off-diagonal stretching-stretching [mdyn Å$^{-1}$]</td>
<td>MN-MX</td>
<td>0.18</td>
<td>0.21</td>
<td>0.28</td>
<td>0.24</td>
<td>0.05</td>
<td>0.18$^a$</td>
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<tr>
<td></td>
<td>MN-NX</td>
<td>0.01</td>
<td>0.02</td>
<td>0.12</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td></td>
<td>MX-MX</td>
<td>0.00</td>
<td>0.07</td>
<td>0.20</td>
<td>0.27</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Off-diagonal bending (in-plane) [mdyn rad$^{-1}$]</td>
<td>MN-MX</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$a$ Fixed values are set for the following force constants: CN stretching: 8.20, off-diagonal stretching-stretching CN-CN: $-0.65$ mdy$n$ Å$^{-1}$, CNC in-plane bending: 1.95, CNM in-plane bending: 1.65, out-of-plane bending at N atom: 0.16, out-of-plane bending at M atom: 0.18, torsion around NM bond: 0.07 mdy$n$ Å rad$^{-2}$; $b$ refers to the constant of trans-interactions PtN-PtN.

As shown in Table 4, for the chloro-, bromo-, and iodo-complexes of cis-configuration, 2, 3 and 4 respectively, the force constants of the PtN bonds decrease in the same order. In the case of the isomers 4 and 5, the force constant of the PtN bond is greater for the trans-complex (5) than for the cis-isomer (4), and the opposite relation is found with respect to the force constants of the PtI bonds. These regularities conform with the concept of trans-influence of the ligands in square-planar Pt(II) complexes [15, 48].

NMR spectra

$^1$H NMR spectroscopic data for PMSA and its complexes are presented in Table 5. The spectra of complexes 4 and 5 in the range of the pyridine protons are compared in Fig. 4. The positions of the signals of the CH$_3$ and NH protons are in accordance with the results for other methanesulfonamide derivatives [7, 8]; the assignment of the latter was confirmed by D$_2$O-exchange. The as-
signification of signals of the pyridine protons conforms with the data for other pyridine derivatives [49, 50] and their platinum(II) complexes [36, 50–52]. In order to verify our assignments and to obtain more accurate values of the coupling constants, a quantum-mechanical analysis of the four-spin pyridine system of PMSA and complexes 1–5 was performed by the LAOCOON iterative programme (root mean square errors below 0.05 Hz). Because of limited solubility, a less resolved spectrum was obtained for 6, and the small coupling constants were not registered. The satellite signals for the protons H(2) and H(6) which arise due to coupling with the 195Pt nucleus deserve special attention. Distinct satellites were observed for compounds 2–5, whereas in the case of 6 only a broadening of the signals was registered. Ha et al. [53] have developed reliable criteria for distinguishing cis- and trans-isomers of platinum(II) complexes, showing that for a vast number of complexes of the type [PtL2X2] (L = pyridine, substituted pyridines; X = Cl, Br, I, NO3), typical values of the JHPl coupling constants are 42 Hz for the cis-isomers, and 32 Hz – for the trans-isomers. For complexes 2–4 the JHPl constants were in the interval of 40 to 44 Hz, whereas for 5 they are 33 and 35 Hz (Table 5, Fig. 4). This confirms the configuration ascribed to complexes 2–5.

Electronic spectra

Taking into account the electronic spectral data for similar complexes [37, 54–56], it could be expected that most of the d-d bands for the PMSA complexes should be masked by charge-transfer bands and by the strong absorption of the pyridine chromophore, which makes the interpretation of their electronic spectra rather difficult. Because of solubility limitations, spectra of aqueous solution were obtained only for PMSA and complex 6, whereas the spectra of the remaining complexes were registered in acetone (below 30000 cm−1). The data of the electronic spectra are summarized in Table 6. In the spectrum of 6 the shoulders at 45500, 39100 and 31700 cm−1 have similar positions as the bands of PMSA, and are tentatively ascribed to intraligand transitions. The remaining bands are ascribed to charge-transfer transitions because of their high extinction coefficients. The positions and the extinction coefficients of the shoulders observed in the spectra of the chloro and bromo complexes 1–3 suggest an assignment to singlet-triplet transitions (probably 3B2 ← 1A1 in C2v) [55, 56]. The bands observed for the iodo complexes 4 and 5 have considerably higher intensity and should be assigned to charge-transfer transitions [54, 55].

### Table 5. 1H NMR spectroscopic data for PMSA and its complexes.

<table>
<thead>
<tr>
<th>Compd. No, solvent</th>
<th>Assignment of the signal, chemical shift [δ, ppm], multiplicity, relative intensity a, b</th>
<th>Coupling constant [J, Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>H(5)</td>
<td>H(4)</td>
</tr>
<tr>
<td>PMSA (CD₃)₂CO</td>
<td>3.04 s</td>
<td>7.36 ddd</td>
</tr>
<tr>
<td>1 (CD₃)₂CO</td>
<td>3H</td>
<td>1H</td>
</tr>
<tr>
<td>2 (CD₃)₂CO</td>
<td>3.19 s</td>
<td>7.52 ddd</td>
</tr>
<tr>
<td>3 (CD₃)₂CO</td>
<td>3.14 s</td>
<td>7.48 ddd</td>
</tr>
<tr>
<td>4 (CD₃)₂CO</td>
<td>3.14 s</td>
<td>7.49 ddd</td>
</tr>
<tr>
<td>5 (CD₃)₂CO</td>
<td>3.14 s</td>
<td>7.51 ddd</td>
</tr>
<tr>
<td>6 (CD₃)₂CO</td>
<td>3.20 s</td>
<td>7.45 ddd</td>
</tr>
<tr>
<td>D₂O</td>
<td>3.01 s</td>
<td>7.48 dd</td>
</tr>
</tbody>
</table>

a Atom numbering according to Fig. 1; b notations: b – broad, d – doublet, dd – doublet of doublets, ddd – threefold doublet, nr – not registered, s – singlet.
Table 6. Electronic spectral data for PMSA and its complexes: wave numbers $[\nu, \text{cm}^{-1}]$ and molar extinction coefficients ($\epsilon, \text{1 mol}^{-1} \text{cm}^{-1}$).

<table>
<thead>
<tr>
<th>Compound No, solvent</th>
<th>$\nu (\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMSA, H$_2$O</td>
<td>45500 (7240), 37700 (3020), 31300 (300)</td>
</tr>
<tr>
<td>1. (CH$_3$)$_2$CO</td>
<td>25500 sh$^a$ (160)</td>
</tr>
<tr>
<td>2. (CH$_3$)$_2$CO</td>
<td>27000 sh (70)</td>
</tr>
<tr>
<td>3. (CH$_3$)$_2$CO</td>
<td>25500 sh (240)</td>
</tr>
<tr>
<td>4. (CH$_3$)$_2$CO</td>
<td>27400 (2030)</td>
</tr>
<tr>
<td>5. (CH$_3$)$_2$CO</td>
<td>29200 (1640)</td>
</tr>
<tr>
<td>6. H$_2$O</td>
<td>48300 (58400), 45500 sh (53600), 43300 sh (45500), 39100 sh (26300), 35100 sh (10600), 31700 sh (4460)</td>
</tr>
</tbody>
</table>

$^a$sh – shoulder.

### Experimental

#### Starting compounds

PMSA was synthesized from methanesulfonyl chloride and 3-aminopyridine by the procedure of Jones and Katritzky [57], and purified with charcoal as described in lit. [12]. The remaining reagents and solvents were commercial products (purum or pro analysi).

#### Preparation of the complexes

**cis-[Pd(PMSA)$_2$Cl$_2$]** (1). 0.24 g (1.39 mmol) of PMSA was dissolved in water (15 ml) and the solution was acidified (pH 4) with acetic acid. This solution was added dropwise with stirring at 20 °C to a filtered solution of K$_2$[PdCl$_4$] (0.20 g, 0.61 mmol) in water (7 ml). Along with the mixing of the reagents a yellow precipitate appeared. One hour later, the precipitate was filtered, washed with water and ethanol, and dried in vacuo over P$_2$O$_5$. Yield: 0.28 g (88%).

**cis-[Pt(PMSA)$_2$Cl$_2$]** (2). The complex was prepared in the same way as 1, but the reaction mixture was left overnight before filtering the pale yellow precipitate, which was washed and dried as above. Yield: 0.31 g (83%).

**cis-[Pt(PMSA)$_2$Br$_2$]** (3). An aqueous solution of K$_2$[PtBr$_4$] [58] was prepared and used in situ: 1.77 g (14.9 mmol) of KBr (7-fold excess) was added to a solution of K$_2$[PtCl$_4$] (0.22 g, 0.53 mmol) in water (9 ml) and the solution was heated at 60–70 °C for 20 min. The dark reddish-brown solution thus obtained was filtered and mixed with 20 °C with stirring with an acidified (pH 4, acetic acid) solution of 0.20 g (1.16 mmol) of PMSA in water (15 ml) to give a yellow precipitate. The reaction mixture was left overnight, after which the precipitate was filtered and treated as above. Yield: 0.33 g (89%).

**cis-[Pt(PMSA)$_2$I$_2$]** (4). Aqueous K$_2$[PtI$_4$] was obtained in situ following lit. [52]: A solution of 0.22 g (0.53 mmol) of K$_2$[PtCl$_4$] in water (3 ml) was mixed with a solution of 0.71 g (4.28 mmol) of KI (2-fold excess) in water (2 ml) and the reaction mixture was left at 20 °C for 20 min. The deep brown solution produced was filtered and mixed with stirring with a solution of 0.20 g (1.16 mmol) of PMSA in water (20 ml) to give a dark yellow precipitate. The reaction mixture was stirred for further 40 min, and the precipitate was filtered and washed with water, methanol and ether. Yield of crude product: 0.38 g (90%). This was dissolved in nitromethane (18 ml) by short heating on a water bath at 80–90 °C. The solution was filtered and...
tetrachloromethane (50 ml) was added. After cooling for 2 h in an ice bath, the fine yellow needles deposited were filtered, washed with tetrachloromethane and dried in vacuo. Yield: 0.16 g (42% of the crude product).

trans-[Pt(PMSA)2]Cl2 (5). 0.36 g (0.38 mmol) of [Pt(PMSA)4]Cl2 (vide infra) and 0.50 g (3.01 mmol) of KI (4-fold excess) were heated in 5 ml of DMF on a boiling water bath until almost everything was dissolved (2–3 min). The turbid solution was filtered and the filter washed with 1 ml of hot DMF. To the deep yellow filtrate, water (30 ml) was added to separate a lemon-yellow precipitate. The precipitate was filtered and washed with water and methanol. Yield of crude product: 0.28 g (93%). The product was dissolved in boiling acetone (ca. 40 ml), the solution was filtered and the filter washed with hot acetone. The filtrate was left to concentrate slowly at 20 °C in the dark. After 2 d, when ca. 7 ml of the solution remained, the yellow needles obtained were filtered, washed with acetone and dried in vacuo. Yield: 0.16 g (57% of the crude product).

[Pt(PMSA)3]Cl2 (6). 0.45 g (0.74 mmol) of cis-[Pt(PMSA)2]Cl2 (vide supra) was added to a boiling solution of 1.02 g (5.92 mmol) of PMSA (4-fold excess) in water (65 ml) and stirred for several minutes until it was almost completely dissolved. The hot solution was filtered and the filter washed with hot water (ca. 10 ml). Ethanol (120 ml) was added to the filtrate and the mixture was left in a refrigerator for 3 h. The white precipitate was filtered and washed with water, ethanol and ether. Yield of crude product: 0.56 g (79%). The product was dissolved in boiling water (65 ml), filtered, and the filtrate left in a refrigerator. The fine colourless needles deposited were filtered, washed with water and ethanol, and dried in vacuo over P2O5. Yield: 0.41 g (73% of the crude product). A partially deuterated specimen was obtained by two-fold recrystallization of the compound from D2O followed by drying in vacuo over P2O5.

Analyses, spectra and calculations

Melting points (uncorrected) were determined with a Boetius heating-plate microscope.

Electric conductivities were measured at 25 °C in a 1 × 10–6 Ω–1 cm–1 range using a Hydromat conductivity meter.

The elemental analyses were performed according to standard microanalytical procedures (Faculty of Chemistry, St. Clement Ochridsky University of Sofia).

IR spectra were recorded in the solid state as CsI (4000–150 cm–1) and KBr disks (4000–400 cm–1) on a Bruker IFS 113 spectrophotometer.

1H NMR spectra were registered on a Bruker DRX-250 spectrometer at 250 MHz in (CD3)2CO or D2O solutions with tetramethylsilane or sodium 3-trimethylsilylpropionate-2,2,3,3-d4 as internal standard.

Electronic spectra were recorded in aqueous or acetone solutions using a Beckman DU-650 spectrophotometer.

The normal coordinate analysis of model fragments of the molecules of the complexes was performed in the harmonic generalized valence force field with the aid of the MOLVIB 6.0 programme of Sundius [59].

The quantum-mechanical analysis (spin Hamiltonian method) of the NMR signals of pyridine protons of the compounds was carried out with the LAOCOON PC iterative programme based on the LAOCN3 algorithm [60].

Acknowledgement

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N. I. Dodoff • Pd(II) and Pt(II) Complexes of N3-Pyridinylmethanesulfonamide