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Raman and resonance Raman spectroscopy of iodoplatinate(II), iodoplatinate(IV) and mixed-valence iodoplatinate(II,IV) salts

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Abstract

The Raman and resonance Raman spectra of a number of new iodoplatinate(II), iodoplatinate(IV) and mixed valence iodoplatinate(II,IV) salts are presented. Previous X-ray structure determination showed that the building blocks of all these compounds consist of PtI_6 octahedra and/or PtI_4 squares, which can be isolated or connected to dimeric units or polymeric chains. The Raman spectra show that the different coordination polyhedra and oxidation states of the platinum atoms have only a small influence on the wavenumbers of bands attributable to the Pt–I stretching modes. Due to the presence of intervalence transitions in the region probed the mixed-valence compounds show stronger resonance effects then the single-valence parent compounds. The resonance Raman spectra are determined not only by A-term activity but also by B-term activity.

Introduction

Halogeno complexes of platinum have been of interest to many scientists since the birth of coordination chemistry and their study has opened a wide field of research. In recent years, special interest has developed in mixed-valence compounds and in attempts to synthesize Pt^{III} compounds. The result of these efforts has been the synthesis of a large number of linear-chain platinum complexes of the Wolffram's Red sort [1] partially oxidized cyanoplatinates of the 'KCP' type such as $K_2Pt(CN)_4X_{0.3}$ (X = Cl or Br) [2] and several genuine Pt(III) complexes [3].

The number of simple halogeno complexes known is small and, in particular, there was little known about iodoplatinates at the beginning of this work. One of the reasons for this is that iodoplatinates may undergo in aqueous solution a number of reactions in which ligand exchange, redox, precipitation and proton transfer processes are involved. Therefore inhomogeneous products are often obtained. At low concentrations of iodide ions platinum iodides such as PtI_4 [4], PtI_3 [5], Pt_3I_8 [6] and β-PtI_2 [7] are formed preferentially. With excess of iodide deep red solutions of iodoplatinates can be prepared and induced to crystallize with suitable cations. Depending on other conditions such as the presence or absence of a reducing agent, Pt^{II}, Pt^{IV} or mixed-valence $Pt^{II,\ IV}$ compounds can be obtained. In this work the main interest lay in studying the possibilities of exchange interactions between Pt^{II} and Pt^{IV} in mixed-valence platinum compounds. By change of the counter cation, each of which has a different spatial requirement, the influence of the metal–metal and metal–iodide interactions on the relevant distances could be probed by Raman and resonance Raman (RR) spectroscopy. As there have been only a very few Raman spectra of iodoplatinates published up till now, it seemed necessary also to try to obtain the spectra of the parent single-valence compounds for comparative purposes.

Experimental

Preparations

$[(CH_3)_nNH_{4-n}]I$ ($n = 1$–3)

Aqueous solutions of the appropriate amines (Merck) were allowed to react with stoichiometric amounts of conc. HI. After the liquid had been removed *in vacuo*, the iodides were recrystallized several times from ethanol–diethyl ether solutions.

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$A_4Pt_2I_{10} \cdot nH_2O$, ($A = Rb$, K, NH_4, N_2H_5, or $NH_2(CH_3)_2$) and $[(CH_3NH_3)_4]Pt_3I_{11}$

An aqueous solution of H_2PtCl_4 was prepared by reduction of H_2PtCl_6 with $[N_2H_6]Cl_2$. After addition of an excess of the appropriate iodide and small amounts of ethanol or methanol the solutions were transferred into a desiccator for crystallization over P_2O_5. After 2–3 days the substances could be isolated. They appeared in the form of thin black needles in the case of $[(CH_3NH_3)_4]Pt_3I_{11}$, bronze needles in the case of $A_4Pt_2I_{10} \cdot nH_2O$ ($A = Rb$, NH_4, K or N_2H_5), and black compact crystals in the case of $[(CH_3)_2NH_2]_4Pt_2I_{10}$.

$A_2Pt_2I_6$ ($A = (CH_3)_nNH_{4-n}$; $n = 1–4$)

These compounds were prepared by adding aqueous solutions of alkylammonium iodide to a freshly prepared H_2PtCl_4 solution. The products precipitated within minutes as black polycrystalline solids. Single crystals could be obtained by recrystallization from methanol.

$A_2Pt_2I_8$ ($A = (CH_3)_nNH_{4-n}$; $n = 2–4$)

Partial oxidation of $A_2Pt_2I_6$ with iodine in methanol, methanol/acetone, or acetone leads to the required compounds, which precipitated as very tiny thin bronze needles.

A_2PtI_6 ($A = (CH_3)_nNH_{4-n}$; $n = 1–4$)

The hexaiodoplatinates were prepared according to Datta [8] by treatment of $H_2PtCl_6 \cdot 6H_2O$ with concentrated aqueous solutions of the alkylammonium iodides.

$[((CH_3)_2NH_2)_3][I_3][PtI_6]$

200 mg $H_2PtCl_6 \cdot 6H_2O$ were dissolved in 2 cm^3 H_2O. Then successively 0.5 cm^3 HI (57%) and 140 mg $(CH_3)_2NH_2$ was added. From a deep red solution a large part of the final product precipitated at once as a black polycrystalline solid. Single crystals of this compound were also prepared as a by-product of the synthesis of $[(CH_3)_2NH_2]Pt_2I_6$.

Instrumentation

The Raman spectra were recorded using a Jobin Yvon spectrometer U1000. Cooling of the samples to 80 K was achieved with an Oxford Instruments liquid-nitrogen cryostat. Excitation radiation was provided by a Spectra Physics krypton-ion laser model 2020-11, a Spectra Physics argon-ion laser model 164-09 and a titanium-sapphire CW tunable laser model 3900 pumped with a 5 W argon-ion laser. Samples were used in the form of pressed disks in $KClO_4$. Laser powers were usually below 100 mW. Slit width 500–800 μm, resulting spectral resolution 3–4 cm^{-1}.

Results

Hexaiododiplatinate(II) salts $A_2Pt_2I_6$ ($A = (CH_3)_n$-NH_{4-n}; $n = 1–4$)

The structures consist of Pt_2I_6 units and the corresponding cation. The anions form edge-shared squares which have nearly D_{2h} symmetry with the exception of $[(CH_3)_3NH]_2Pt_2I_6$, where a deviation from planarity of this group has been found (dihedral angle 11.4° [9]). By contrast to earlier results on compounds of this type [10] the terminal Pt–I distances are invariably less than the bridging Pt–I distances (Pt–I_b); moreover the I_b–Pt–I_b angles are always near 85°, while the exocyclic angles lie round 95° (see Fig. 1). According to the size of the cation different arrangements of the building groups are found (cf. Figs. 1 and 2).

Raman spectra

The Raman spectra of the four different salts of the $[Pt_2I_6]^{2-}$ ion are very complicated and cannot be fully interpreted. The solid state spectra show differences in the intensities of some bands as compared to those reported by Goggin [11] for spectra of this anion in solution. There the strongest band (at 160 cm^{-1}) was assigned to the totally symmetric stretching mode, ν_2. Other strong bands were found at 93 and 145 cm^{-1}. In the crystalline state the intensity of the band at 160 cm^{-1} is much less than that near 145 cm^{-1} (see Fig. 3, Table 1). In the region between 115–130 cm^{-1} a very intense band, which shows up to four harmonics, is found in all spectra except that of $[(CH_3)_3NH]_2Pt_2I_6$ for which the edge-shared squares are not coplanar. It is in the same region as progressions have been found for mixed-valence iodoplatinates. Polarization

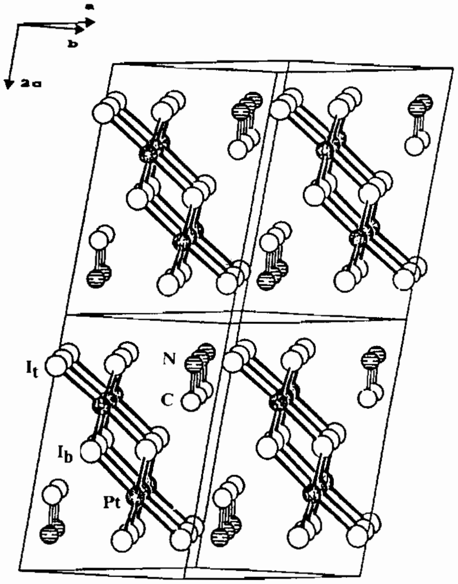

Fig. 1. Arrangement of Pt_2I_6 groups in $(CH_3NH_3)_2Pt_2I_6$.

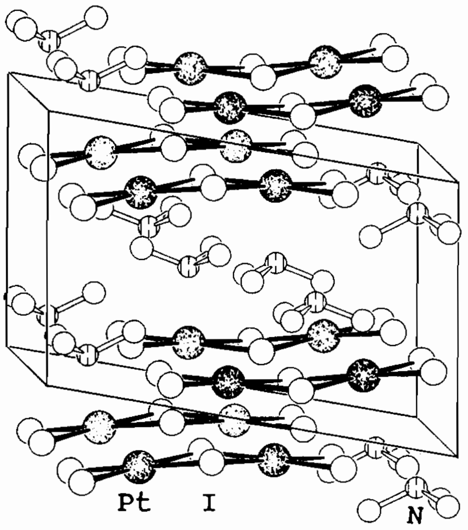

Fig. 2. Unit cell of $[(CH_3)_3NH]_2Pt_2I_6$. The Pt_2I_6 groups show considerable deviation from planarity.

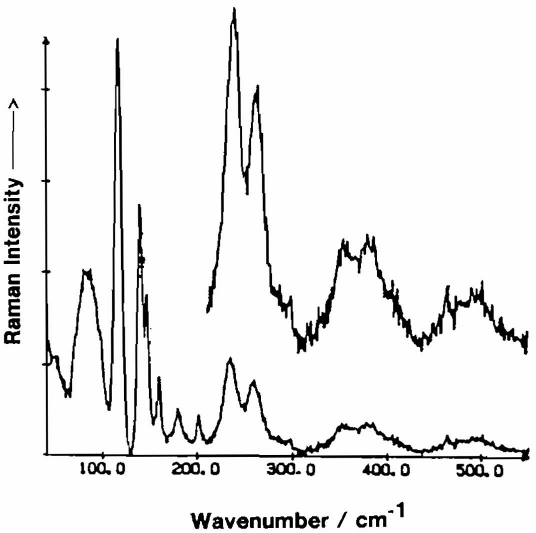

Fig. 3. Raman spectrum of $(CH_3NH_3)_2Pt_2I_6$.

TABLE 1. Raman data on salts of $[Pt_2I_6]^{2-}$ ($\lambda_0 = 800$ nm)

CH_3NH_3	$(CH_3)_2NH_2$	$(CH_3)_3NH$	$(CH_3)_4N$	Assignment
83 m			114 m	
117 vs	128 vs	125 w, br	127 vs	ν_1
	140 w			
140 s	149 s	145 vs	144 m	ν_3
148 sh				
160 w	160 s	161 s	151 vs	ν_2
180 w			160 m	
202 w	197 w	199 w	196 w	
			233 w	
236 m	252 w		254 vw	$2\nu_1$
259 m	278 w			$\nu_1 + \nu_3$
352 wm				$3\nu_1$
378 wm				$2\nu_1 + \nu_3$
400 sh				$2\nu_1 + \nu_2$
468 w				$4\nu_1$
492 w, br				$3\nu_1 + \nu_3$

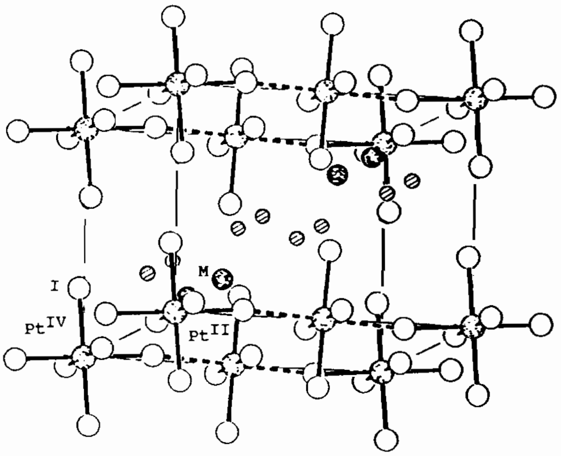

Fig. 4. Linear halogen-bridged chains of $Pt^{IV}I_6Pt^{II}I_4$ groups in the structures of $M_4Pt_2I_{10} \cdot 4H_2O$ (M = K, Rb, NH_4 or N_2H_5).

studies on the spectra in solution rule out the possibility that the progression-forming mode might be totally symmetric, and hence the B-term mechanism must be responsible for the resonance enhancement of this series of bands.

Mixed-valence iodoplatinate(II,IV) salts

$A_4Pt_2I_{10} \cdot nH_2O$ (A = Rb, Cs, K, NH_4, or N_2H_5), $n = 2$–4

The structures of these compounds consist of linear iodo-bridged chains of alternating $Pt^{IV}I_6$ octahedra and $Pt^{II}I_4$ squares (Fig. 4) [12]. As has been shown for a large number of similar compounds, the Raman spectra usually exhibit strong resonance effects with a long overtone progression in the symmetric I–Pt^{IV}–I mode, ν_1' especially for compounds with cationic and neutral chains [1]. For compounds with anionic chains there have been few investigations made up to now. In an earlier work it was found that $K_4Pt_2I_{10} \cdot 4H_2O$ yields a relatively weak RR spectrum, only three harmonics of ν_1' being evident with 799.3 nm excitation [13]. With the aid of a tunable IR-laser these spectra can now be improved upon. It turns out that, besides five harmonics of ν_1', overtones of the non-totally symmetric stretching mode ν_2, and combination tones between ν_1' and ν_2 occur (see Fig. 5, Table 2). These results are similar to those for $Cs_2[Pt_2(NO_2)_2(NH_3)_2Br_6]$, which likewise contains an anionic chain and whose RR spectrum displays several subsidiary progressions [14]. Such spectral features are ascribed to the more extended

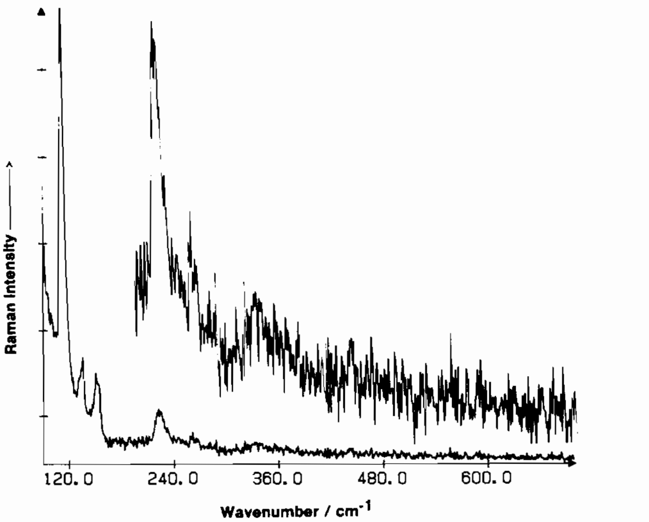

Fig. 5. Raman spectrum of the linear-chain compound $K_4Pt_2I_{10}\cdot 2H_2O$. $\lambda_0 = 676.4$ nm.

TABLE 2. Wavenumbers (cm^{-1}) of Raman bands for $A_4Pt_2I_{10}\cdot nH_2O$ compounds ($\lambda_0 = 676.4$ and 800 nm)

$(N_2H_5)_4Pt_2I_{10}\cdot 2H_2O$		$K_4Pt_2I_{10}\cdot 4H_2O$		Assignment
676.4	800.0	676.4	800.0	
113 m	110 vs	110 s	110 vs	ν'_1 (PtI_6-PtI_4-chain)
126 vs	129 vs	130 vs	130 m	ν_2 (PtI_6^{2-})
148 s	151 s	149 vs	151 s	ν_1 (PtI_6^{2-})
176 vw		177 vw	173 w	ν_3 (PtI_6^{2-})
226 w	221 m		221 m	$2\nu'_1$
259 w	259 m		263 w	$\nu'_1+\nu_1$
		262 w		$2\nu_2$
277 w	280 m			$\nu_1+\nu_2$
	332 w		333 m	$3\nu'_1$
351 vw	350 w	347 w	351 vw	$2\nu'_1+\nu_2$
		371 vw	369 vw	$\nu'_1+2\nu_2$
431 w		430 vw	426 vw	$2\nu_1+\nu_2$
	440 w		435 w	$4\nu'_1$
	455 w	448 w	453 w	$3\nu_1$
463 m	464 m	463 s	464 s	ν'_2 (ClO_4^-)
		473 w		$3\nu'_1+\nu_1$
			483 w	$3\nu_1+\nu_2$
501 vw				$4\nu_2$
548 vw				$2\nu_1+2\nu_2$
	545 vw		546 vw	$5\nu'_1$
556 vw				$3\nu_1+\nu'_1$
567 vw				$3\nu_1+\nu_2$
581 vw				$4\nu_1$
618 vw				$\nu'_1+4\nu_2$

vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

charge delocalization in these compounds. The excitation profiles of the three main bands of $(N_2H_5)_4Pt_2I_{10}\cdot 2H_2O$ and $K_4Pt_2I_{10}\cdot 4H_2O$ in the range between 514.5 and 830 nm (Fig. 6) show different behaviour.

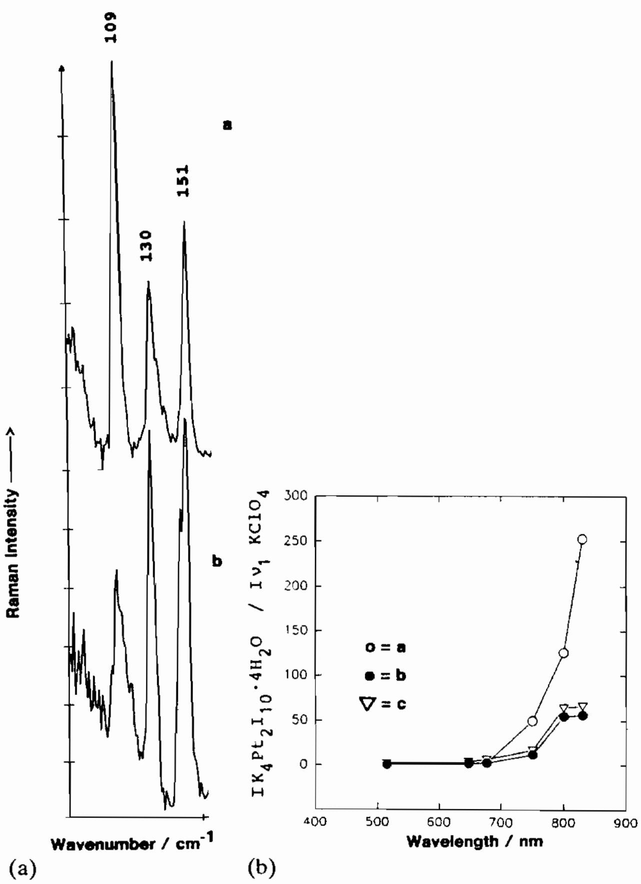

Fig. 6. (a) Raman spectra of $K_4Pt_2I_{10}\cdot 4H_2O$ at different excitation wavelengths: a, $\lambda_0 = 800$ nm, b, $\lambda_0 = 676.4$ nm. (b) Excitation profile of $K_4Pt_2I_{10}\cdot 4H_2O$: a, band at 109 cm^{-1}, b, band at 130 cm^{-1}; c, band at 151 cm^{-1}.

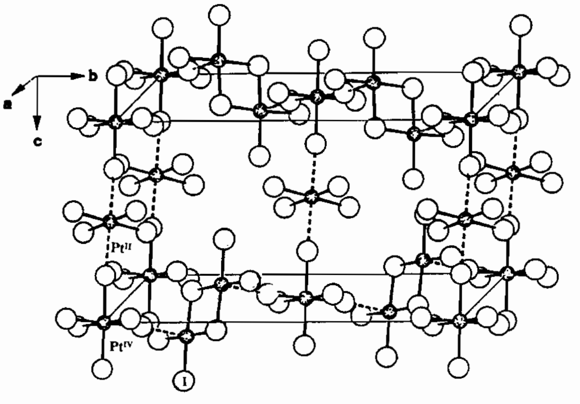

Fig. 7. Structure of the mixed-valence compound $(CH_3NH_3)_4Pt_3I_{11}$. Linear halogen-bridged chains and Pt_2I_6 units form the building blocks. The cations have been left out for clarity.

[(CH₃NH₃)₄]Pt₃I₁₁

Like the $M_4Pt_2I_{10}\cdot nH_2O$ salts this compound also consists of linear iodo-bridged chains of PtI_6 octahedra and PtI_4 squares but, in addition, it contains $Pt_2I_6^{2-}$ ions which consists of edge-shared coplanar PtI_4 squares [15] (see Fig. 7). The Pt–I distances within the octahedral

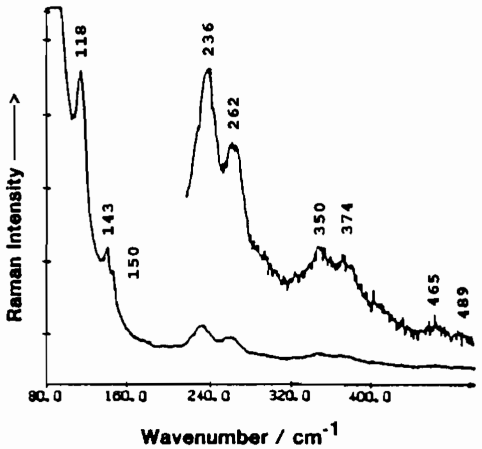

Fig. 8. Raman spectrum of $(CH_3NH_3)_4Pt_3I_{11}$.

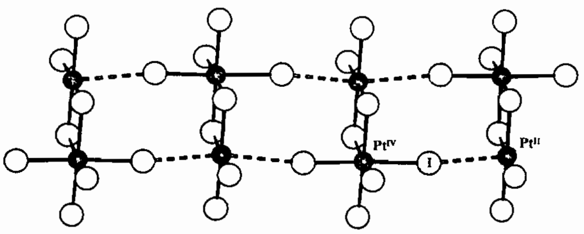

Fig. 9. Linear chains of $[Pt_2I_8]^{2-}$ anions in $[(CH_3)_2NH_2]_2Pt_2I_8$.

and square planar building groups correspond well to those in similar compounds [6, 9]. Typical values are Pt–I_{oct} = 2.67–2.68 Å, Pt–I_{square} = 2.58–2.59 Å, Pt^{II}–I–Pt^{IV} = 3.26, 2.67 Å. There is also a rather short Pt–I distance of 3.35 Å between one equatorial I atom of the octahedral groups and a platinum atom of the double squares which leads to a strongly elongated square prismatic coordination of the Pt^{II} ions within the Pt_2I_6 units.

The Raman and RR spectra of this compound are assigned in a similar way to those for the $M_4Pt_2I_{10} \cdot nH_2O$ compounds (see Table 2, Fig. 8) which contain linear chains of the same kind, and those of the hexaiododiplatinate(II) salts $A_2Pt_2I_6$. Only four harmonics of ν_1 are evident, which may be a consequence of the additional cross connections between the linear chains and the Pt_2I_8 units.

Octaiododiplatinate(II,IV) salts $A_2Pt_2I_8$ $(A = (CH_3)_nNH_{4-n},\ n = 2–4)$

Anions of square planar PtI_4 units which share one equatorial edge with an octahedral PtI_6 group are the building blocks of these structures (Fig. 9) [16]. Here mixed-valence units are more closely connected than in the compounds characterized above. Depending on the cation size these units are either arranged in linear chains as in $[(CH_3)_2NH_2]_2Pt_2I_8$ or as isolated groups as in $[(CH_3)_4N]_2Pt_2I_8$. The Raman spectra of these compounds are very similar to those of the other compounds investigated here, so that the reduced symmetry of the Pt_2I_8 group does not lead to an increased number of Raman bands. According to factor group analysis there would be, without correlation coupling, 24 Raman bands expected for the Pt_2I_8 skeleton having C_{2v} symmetry, viz. $9a_1$, $3a_2$, $7b_1$, $5b_2$ which, with the exception of a_2, are all also IR active. In reality the spectra show the pattern of bands typical of isolated octahedral or square planar groups (Fig. 10). The bands near 150 cm^{-1} were accordingly assigned to the totally symmetric stretching mode and that at 135 cm^{-1} to a non-totally symmetric one. There is, as for the linear chain compounds, a band at lower wavenumbers (116, 124, 127 cm^{-1}) which could be assigned to the symmetric stretching mode of the chain but could also result from a splitting of the e_g mode caused by symmetry reduction. The intensity of this band is larger for $[(CH_3)_2NH_2]_2Pt_2I_8$ and $[(CH_3)_3NH]_2Pt_2I_8$, where interaction between the anions is possible by chain formation (cf. Fig. 9), than for $[(CH_3)_4N]_2Pt_2I_8$ where the $Pt_2I_8{}^{4-}$ anions are isolated from each other. The shift of this band from 116 cm^{-1} for the dimethylammonium salt to 127 cm^{-1} for the tetramethylammonium salt shows that, with diminishing intermolecular interactions, the intramolecular Pt–I bonds gain strength.

$[(CH_3)_2NH_2]_4Pt_2I_{10}$

This mixed-valence compound belongs to class I according to the Robin and Day scheme [17]. The structure consists of isolated $Pt^{IV}I_6$ octahedra and $Pt^{II}I_4$ squares, which are arranged as shown in Fig. 11 [18]. The shortest intermolecular Pt–I distance here is 5.46 Å compared to that for the class II compound $(N_2H_5)_4Pt_2I_{10} \cdot 2H_2O$ of 3.25 Å. An increase in cation size leads here to the same effect as with the octaiododiplatinates, viz. the Pt^{IV}–I–Pt^{II} bridges disappear. In the Raman spectrum two broad strong bands at 127 and 148 cm^{-1} are assigned to the fundamentals ν_2 and ν_1, respectively, of the PtI_6 octahedron. Here a possible electronic Raman effect may be detected. Progressions reaching to $3\nu_2$ and combination tones are seen in the RR spectrum (cf. Fig. 12). These progressions appear to arise via a B-term mechanism because they stem from non-totally symmetric vibrations. Another explanation would be that, by symmetry reduction in the excited state or through Jahn–Teller coupling, A-term activity of non-totally symmetric states occurs. However, this can be ruled out because in this case there should also be A-term activity of the totally symmetric mode. The weak band at 182 cm^{-1} can be assigned to the normally Raman inactive antisymmetric stretching mode, ν_3, which has become active through symmetry reduction.

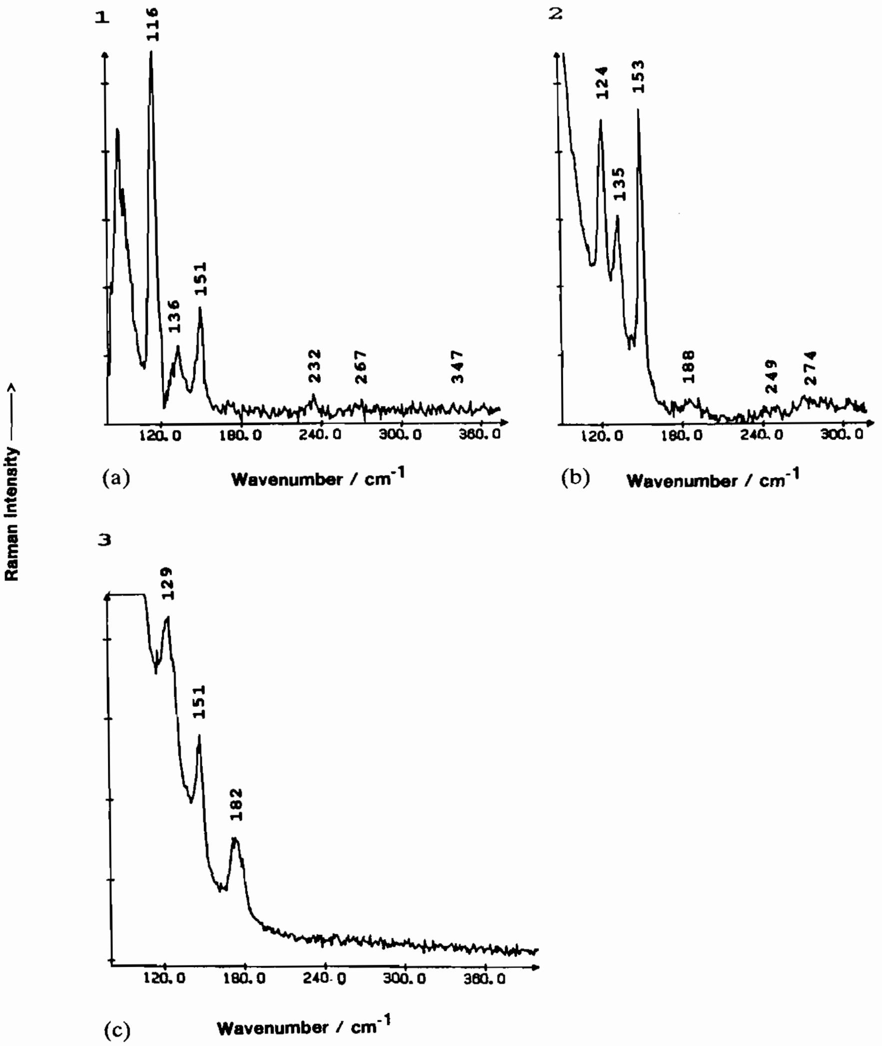

Fig. 10. Raman spectra of: (a) $[(CH_3)_2NH_2]_2Pt_2I_8$, (b) $[(CH_3)_3NH]_2Pt_2I_8$, (c) $[(CH_3)_4N]_2Pt_2I_8$.

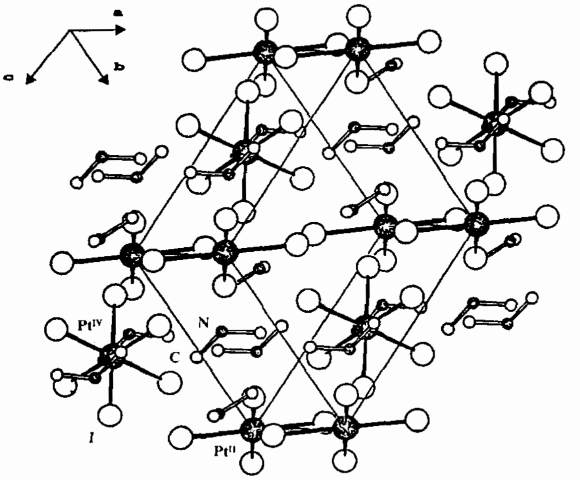

Fig. 11. $[(CH_3)_2NH_2]_4Pt_2I_{10}$ a mixed-valence compound where PtI_6 and PtI_4 units exist independently of each other.

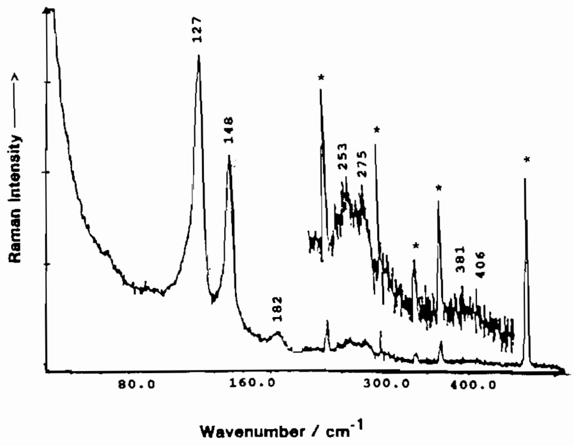

Fig. 12. Raman spectrum of $[(CH_3)_2NH_2]_4Pt_2I_{10}$ (* = plasma lin or bands from matrix material).

Hexaiodoplatinates(IV) $[(CH_3)_nNH_{4-n}]_2PtI_6$, n = 1–4

These compounds crystallize in distorted K_2PtCl_6-type structures with isolated PtI_6^{2-} groups [10, 19, 20, 21]. The Raman spectra of all four compounds can be interpreted on the basis of slightly distorted PtI_6 octahedra and the wavenumbers of the analogous modes differ only slightly from each other and are also in agreement with those of similar compounds previously investigated [22] (Fig. 13, Table 3).

$[(CH_3)_2NH_2)]_3[I_3]PtI_6$

This compound can be described as a double salt with the formula $[(CH_3)_2NH_2)_2]PtI_6 \cdot [(CH_3)_2NH_2]I_3$. The anionic framework consists of PtI_6 and I_3 groups [10] (Fig. 14). There are close non-bonded I–I contacts of 3.56 Å between terminal I atoms of the I_3 groups and iodine atoms of the PtI_6 octahedra. The I_3 groups and the *trans* I–Pt–I groups of the octahedra are lined up alternately to form a linear chain. The Raman spectra obtained with an excitation wavelength of 800 nm show a rich series of overtone and combination tone progressions involving ν_1 (a_{1g}) and ν_2 (e_g) of PtI_6^{2-} as well as ν_1' of I_3^- (Fig. 15, Table 4). Comparison with the RR spectra of CsI_3 [23] shows that the isolated I_3^- ion at this excitation wavelength should not yield a RR spectrum because its absorption maximum lies near 488 nm; at 647.1 nm it does not display a resonance effect. A reasonable explanation for the stronger resonance effects compared to those displayed by other

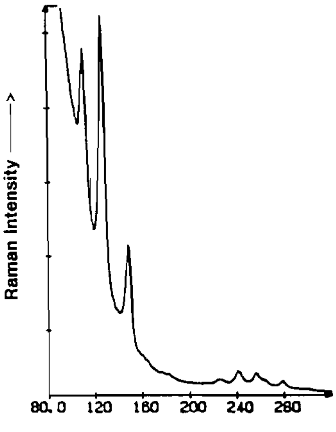

Fig. 13. Raman spectrum of $[(CH_3)_2NH_2]_2PtI_6$.

TABLE 3. Raman data on salts of $[PtI_6]^{2-}$ (λ_0 = 800 nm)

CH_3NH_3	$(CH_3)_2NH_2$	$(CH_3)_3NH$	$(CH_3)_4N$	Assignment
ca. 112 w	114 m		117 w	$\nu_5(t_{2g})$ or lattice
129 s	130 vs	128 s	135 vs	$\nu_2(e_g)$
148 vs	152 m	147 m	151 vs	$\nu_1(a_{1g})$
183 w	180 vw	181 w	182 w	$\nu_3(t_{1u})$
	229 vw			2×114
	245 w			$\nu_2+\nu_5$
	261 w			$2\nu_2$
	266 vw			$\nu_1+\nu_5$
		276 w		$\nu_1+\nu_2$
		294 w		$2\nu_1$

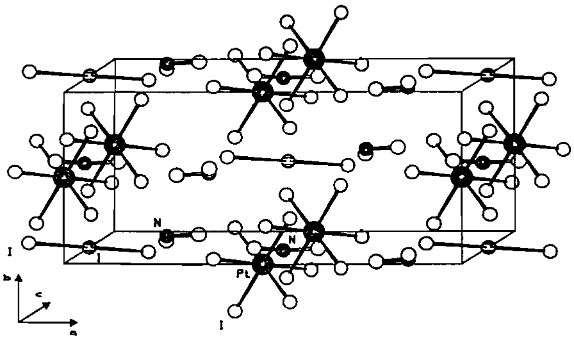

Fig. 14. Unit cell of $[(CH_3)_2NH_2]_3[I_3]PtI_6$. The I–I–I$^-$ groups and I–Pt–I groups form linear chains in the [101] direction.

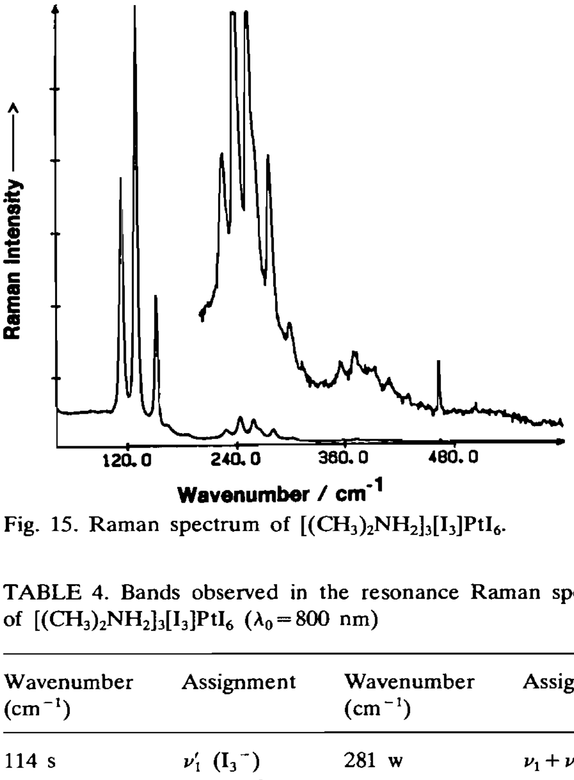

Fig. 15. Raman spectrum of $[(CH_3)_2NH_2]_3[I_3]PtI_6$.

TABLE 4. Bands observed in the resonance Raman spectrum of $[(CH_3)_2NH_2]_3[I_3]PtI_6$ (λ_0 = 800 nm)

Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
114 s	ν_1' (I_3^-)	281 w	$\nu_1+\nu_2$
130 vs	ν_2 (PtI_6^{2-})	302 w	$2\nu_1$
152 m	ν_1 (PtI_6^{2-})	357 vw	$2\nu_1'+\nu_2$
183 w		373 vw	$\nu_1'+2\nu_2$
227 w	$2\nu_1'$	393 vw	$3\nu_2$
244 wm	$\nu_1'+\nu_2$	411 vw	$\nu_1'+2\nu_1$
259 wm	$2\nu_2$	432 vw	$2\nu_1+\nu_2$
265 w	$\nu_1'+\nu_1$	445 vw	
		453 vvw	$3\nu_1$
		505 vvw	$\nu_1'+3\nu_2$

vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

hexaiodoplatinates must lie in the structural features mentioned above. The relatively short intermolecular I–I contacts seem to foster exchange interaction between the I_3 and the PtI_6 groups such that, on excitation to the resonant state, significant structural changes to both anions take place.

Discussion

The results presented in this work give for the first time an overview on the Raman spectra of a number of iodoplatinates in the solid state. It turns out that the wavenumbers of the symmetric Pt–I valence bands are almost independent of the geometry of the coordination polyhedra (octahedron, square or combination of these units). The values found for ν_1 (a_{1g}), lie between 148 and 153 cm^{-1}, in agreement with the reported value for PtI_6^{2-} at 150 cm^{-1} [22]. Apparently there is not much difference in bonding strength either between octahedral and square planar units or between terminal and bridging Pt–I bonds. This is in contrast to the chloro and bromo compounds, for which a small difference between the ν_1 bands of PtX_6^{2-} and PtX_4^{2-} is evident, viz. ν_1 $PtCl_6^{2-}$ 348 cm^{-1} [24], ν_1 $PtCl_4^{2-}$ 330 cm^{-1}, ν_1 $PtBr_6^{2-}$ 213 cm^{-1} [25], ν_1 $PtBr_4^{2-}$ 208 cm^{-1} [26]. The results show that on changing from chloro to iodo compounds the strong polarizing power of the Pt^{IV} cation becomes less effective as the spatial requirements of the anions increase.

The RR effect which is found with the linear-chain compounds has previously been associated with an intervalence transition of wavelengths longer than 800 nm [14]. This is confirmed now with the excitation profile of $K_4Pt_2I_{10}\cdot 4H_2O$, for which the maximum intensity of the band at 109 cm^{-1} had still not been reached with $\lambda_0 = 830$ nm. Comparison of the RR spectra of these compounds with those of iodo compounds with neutral chains, e.g. $Pt_2(en)_4I_2$, en = 1,2-diaminoethane, shows that the former display a much shorter overtone progression in the ν_1 mode, but more intense subsidiary progressions (arising from the equatorial Pt–I vibration which usually occurs around 120 cm^{-1}) than the latter. The excitation profile of this band is different from that of ν_1 and its maximum lies at 800 nm. With growing asymmetry of the Pt^{II}–I–Pt^{IV} bridges, the resonance effect diminishes, as is apparent in the series $(N_2H_5)_4Pt_2I_{10}\cdot 2H_2O$, $(MeNH_3)_4Pt_3I_{11}$ and $((CH_3)_nNH_{4-n})_2Pt_2I_8$ ($n = 2$–4).

Hamaguchi *et al.* [22] observed a RR effect for PtI_6^{2-} in solution with excitation in the range between 457.9 and 514.5 nm. Weak subsidiary progressions were found which have been ascribed to B-term activity [26, 27]*. The present investigation was mainly conducted with excitation wavelengths of 800 nm. Since some of the progression-forming modes arise from non-totally symmetric vibrations the B-term mechanism seems to be in operation here also, especially since these modes in many cases give rise to more intense bands than do the totally symmetric ones. It is concluded that on electronic excitation almost no change of molecular symmetry occurs, and that vibronic coupling via ν_2 of the low lying electronic states of the ion is responsible for the resonance enhancement of the ν_2 band.

The spectra of the hexaiododiplatinates(II) show marked relationships between the intensities of Raman bands and the geometric shape of the anions. As mentioned above, the planar Pt_2I_6 units give rise to a strong band between 117 and 127 cm^{-1} which shows overtone progressions, while in solution and with $[(CH_3)_3NH)]_2Pt_2I_6$ where the edge-shared PtI_4 squares are not coplanar, this band was not found. So planarity, or in other words a particular orientation of atomic orbitals relative to each other, turns out to be essential for the resonance effect, especially if the B-term mechanism is in operation.

Supplementary material

Detailed information concerning the crystal structures is available on request to author H. W. Rotter.

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*An A-term contribution to the transition polarizability arises when the resonant electronic transition is electric dipole allowed; it leads to enhancement to the intensities of bands arising from totally symmetric modes and their overtones and combination tones. A B-term contribution to the transition polarizability arises from vibronic coupling of the resonant state to other excited states. It leads to resonance enhancement to bands arising from fundamentals alone (usually non-totally symmetric ones), the selection rules being constrained by the symmetries of both resonant and excited states.

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