

be used to indicate the conformational preference of phenyl groups as well as methyl groups on diamine chelates. For the complexes reported here, conformational influences of phenyl groups and methyl groups are quite smaller.

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**Registry No.**  $\alpha$ -Deuterio-(*R,S*)-alanine, 31024-91-6; pn-*d*<sub>1</sub>, 67031-29-2; *S*-pn-*d*<sub>2</sub>, 67031-30-5; K[Co(CN)<sub>4</sub>(*R*-phenen)], 67031-32-7; [Pt(*S*-pn-*d*<sub>2</sub>)<sub>2</sub>]Cl<sub>2</sub>, 67031-33-8; [Pt(*S*-pn)<sub>2</sub>]Cl<sub>2</sub>, 17830-46-5; [Pt(*S,S*-bn)<sub>2</sub>]Cl<sub>2</sub>, 67031-34-9; [Pt(NH<sub>3</sub>)<sub>2</sub>(pn-*d*<sub>1</sub>)]Cl<sub>2</sub>, 67031-35-0; [Pt(en)((-)-*D*-stien)]Cl<sub>2</sub>, 67144-40-5; [Pt(en)(*ms*-stien)]Cl<sub>2</sub>, 67031-36-1; [Pt(en)(*R*-phenen)]Cl<sub>2</sub>, 67031-37-2.

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## Electronic and Resonance Raman Spectra of One-Dimensional Mixed-Valence Platinum-Ethylamine Complexes at Ca. 80 K

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The resonance Raman spectra of the mixed-valence complexes [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>X<sub>2</sub>]X<sub>4</sub>·4H<sub>2</sub>O, where X = Cl or Br, and [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>X<sub>2</sub>]X<sub>4</sub>, where X = Br or I and etn = ethylamine, have been recorded at ca. 80 K. The spectra are characterized by the appearance of intense progressions  $\nu_1\nu_1$  and  $\nu_n + \nu_1\nu_1$ , where  $\nu_1$  is the symmetric X-Pt<sup>IV</sup>-X stretching mode. The  $\nu_1\nu_1$  progression reaches at most to  $\nu_1 = 16$ , while the subsidiary progressions are rather shorter and less intense; these data permit various spectroscopic constants to be calculated. The nature of the observed progressions is discussed in terms of distortions of the structures of the complexes in the excited state, the principal geometric change being an increase in the platinum(IV)-halogen bond length. The relation between the maxima of the excitation profiles of the  $\nu_1$  band and those of the resonant mixed-valence bands is also outlined.

## Introduction

A vast amount of research has been and is being carried out on a wide range of materials which have anisotropic physical properties, such as organic and inorganic one-dimensional materials.<sup>1</sup> Of the many techniques which have been applied to the study of such compounds, resonance Raman (RR) spectroscopy has, so far, played only a small but nevertheless useful part.<sup>2</sup> In this paper we intend to show how RR spectroscopy can be used as an indicator of geometrical changes in such a system, caused by a transition from the ground to an excited electronic state. The compounds which we have investigated are mixed-valence compounds of platinum which contain four-coordinate platinum(II) and six-coordinate platinum(IV) units arranged alternately in chains (Figure 1A). The platinum(IV) complex contains two trans halogen atoms oriented along the chain axis, and the remaining coordination sites are occupied by ethylamine molecules. The platinum(II) complex contains four coordinated ethylamine molecules, and the occupied  $d_{z^2}$  orbital of the platinum atom is also directed along the chain axis. The relative positions of the highest filled and lowest unfilled orbitals are depicted in Figure 2. From the diagram it can be seen that the lowest axially polarized mixed-valence transition involves the transfer of an electron from the filled  $5d_{z^2}$  orbital of the Pt(II) complex to the empty

$5d_{z^2}$  orbital of the Pt(IV) complex. Day has reported<sup>3</sup> the 4 K single-crystal electronic absorption spectrum of Wolfram's red salt (WR), [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>4</sub>·4H<sub>2</sub>O (etn = ethylamine), which apparently has axially polarized mixed-valence transitions in the 17 500–21 000-cm<sup>-1</sup> region. The room temperature RR spectrum of this complex consists<sup>4</sup> of a progression in the  $\nu(\text{Cl-Pt}^{\text{IV}}\text{-Cl})$  axial breathing mode ( $\nu_1$ ) which reaches  $9\nu_1$ . A rather similar behavior has been observed<sup>5</sup> for Reihlen's green (RG), which is the bromo analogue of WR. Recent technical advances have enabled us now to record RR spectra of complexes at ca. 80 K with an oscillating laser beam to avoid the deleterious effects of thermal heating of the sample. Spectra so obtained on WR and RG are much more detailed and spectacular than those obtained at room temperature, and they open the way to presenting a discussion of the observed progressions in terms of distortions of the structure of the complexes in the excited state. Related results are also presented on the anhydrous form of Reihlen's green, (ARG) and on the anhydrous iodide recently reported by Textor and Stieger<sup>6</sup> (TSI), viz., [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>X<sub>2</sub>]X<sub>4</sub>, X = Br or I.

## Experimental Section

**Preparation of Complexes.** WR was prepared by an improvement to the method of Reihlen and Flohr.<sup>7</sup> A solution containing 1 g of

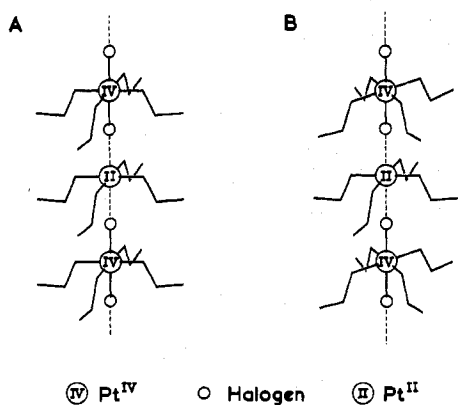


Figure 1. Structure of the complexes  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{X}_2]\text{X}_4 \cdot 4\text{H}_2\text{O}$ , etn = ethylamine and  $\text{X} = \text{Cl}$  or  $\text{Br}$ , and  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{X}_2]\text{X}_4$ ,  $\text{X} = \text{Br}$  or  $\text{I}$ .

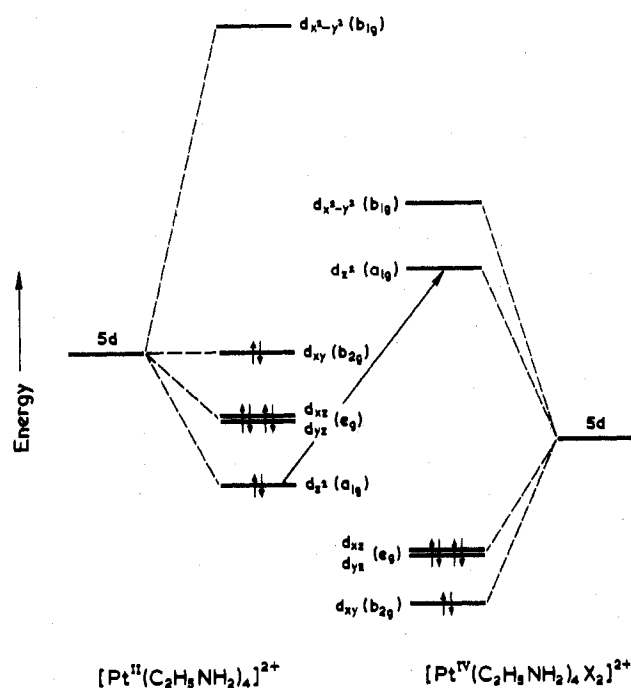


Figure 2. Diagram showing the relative positions (schematic) of the highest filled and lowest unfilled molecular orbitals in  $[\text{Pt}(\text{etn})_4]^{2+}$  and  $[\text{Pt}(\text{etn})_4\text{X}_2]^{2+}$  complexes. The lowest axially polarized mixed-valence transition is indicated by an arrow.

$\text{K}_2[\text{PtCl}_4]$  and  $0.38 \text{ cm}^3$  of 70%  $\text{EtNH}_2/\text{H}_2\text{O}$  in  $10 \text{ cm}^3$  of water was left to stand overnight. This always produced a blackish brown solution and a black solid. The heterogeneous mixture was then treated with  $2\text{--}3 \text{ cm}^3$  of 30%  $\text{H}_2\text{O}_2$  solution, heated for  $10\text{--}15 \text{ min}$  on a steam bath and then filtered to remove the small amount of black solid which had not reacted. The filtrate was treated with an excess of 70% ethylamine solution and heated on a steam bath almost to dryness. The resulting slurry of a light brown solid was stirred with  $15 \text{ cm}^3$  of 4 M  $\text{HCl}$  solution for a few minutes and the resulting Wolfram's red salt was then filtered off; yield  $\approx 50\%$ .

The hydrated bromo complex (Reihlen's green) was obtained by treating Wolfram's red salt with cold concentrated  $\text{HBr}$  solution, the anhydrous form by using hot concentrated  $\text{HBr}$  solution. The anhydrous iodide was prepared by the method of Textor and Stieger.<sup>6</sup>

**Instrumental Details.** Electronic spectra were recorded at ca. 80 K on a Cary 14 (Applied Physics Dewar) spectrometer, the samples being dispersed in potassium halide pressed disks. Raman spectra were recorded using a Spex 1401 double monochromator with  $1200\text{-line mm}^{-1}$  Bausch and Lomb gratings in conjunction with Coherent Radiation Model 52  $\text{Kr}^+$  and Model 12  $\text{Ar}^+$  ion lasers. Detection was by standard photon-counting techniques, employing an RCA C31034 photomultiplier tube. Low-temperature spectra were

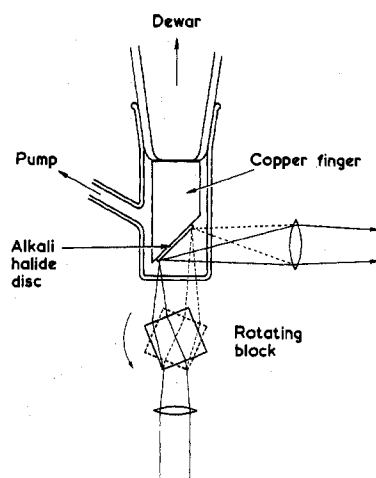


Figure 3. Device which permits a laser beam to be flicked rapidly across the surface of a sample which is held at liquid-nitrogen temperature.

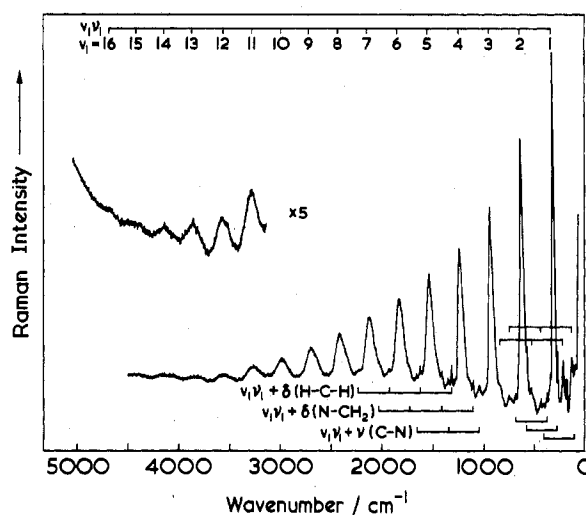


Figure 4. Resonance Raman spectrum of the complex  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  recorded at ca. 80 K using 514.5-nm excitation. Spectral slit width  $\approx 2 \text{ cm}^{-1}$ .

recorded using a device illustrated in Figure 3. This involves a liquid-nitrogen cell attached to which is a  $\text{KX}$  disk containing the compound under study; a glass block rotating at ca. 1500 rpm refracts the laser beam rapidly across the surface of the sample. The device is thus a significant development of earlier ones for sample handling in Raman spectroscopy.<sup>8-10</sup>

All band intensities were corrected for the spectral response of the instrument. The best spectra were obtained when the laser line power was kept below 200 mW.

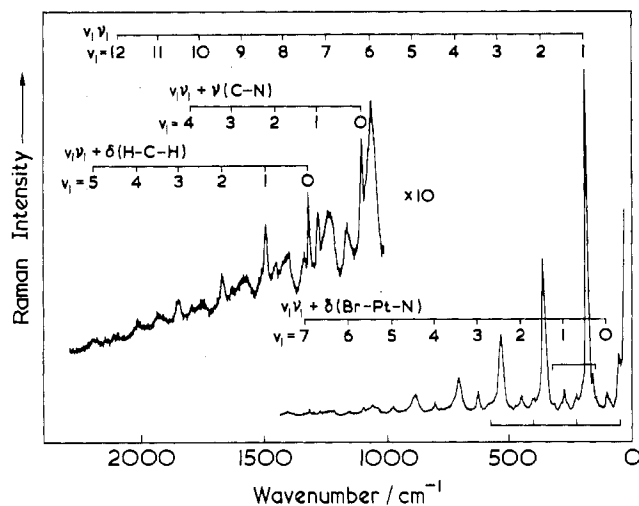
## Results and Discussion

**(a) Wolfram's Red and Reihlen's Green.** The RR spectrum of WR at ca. 80 K is much more detailed than that at room temperature. The dominant features are bands which are part of the  $\nu_1\nu_1$  progression, where  $\nu_1$  is the  $\text{X-Pt}^{\text{IV}}\text{-X}$  symmetric stretching mode; this progression is observed to reach  $\nu_1 = 16$ . In addition to the  $\nu_1\nu_1$  progression, however, many other weaker bands appear in the spectrum and virtually all of these are part of progressions in  $\nu_1$  based on one quantum of another fundamental  $\nu_n$ , i.e.,  $\nu_n + \nu_1\nu_1$ . Four members of the  $\delta(\text{HCH}) + \nu_1\nu_1$  progression, four members of the  $\delta(\text{NCH}_2) + \nu_1\nu_1$  progression, and three members of the  $\nu(\text{CN}) + \nu_1\nu_1$  progressions have been identified; in addition, members of at least five other progressions are evident in the spectrum, but the enabling mode has not been identified in these cases (Figure

**Table I.** Wavenumbers and Assignments of the Bands in the Resonance Raman Spectrum of the Complex  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}^{a,b}$ 

$\tilde{\nu}/\text{cm}^{-1}$	assignment	$\tilde{\nu}/\text{cm}^{-1}$	assignment
95.5		1094	} $\nu(\text{CN}), \nu_2$
123.5		1098	
131.5		1154	$\delta(\text{NCH}_2), \nu_3$
177.6		1222	$4\nu_1$
201.9		1308	} $\delta(\text{HCH}), \nu_4$
215.8		1345	
260.6		1405	$\nu_1 + \nu_2$
266.4		1459	$\nu_1 + \nu_3$
292.3	} $\delta(\text{CIPtN})$	1524	$5\nu_1$
296.8		1617	} $\nu_1 + \nu_4$
308.3	$\nu_{\text{sym}}(\text{CIPtCl}), \nu_1$	1650	
341.9		1767	$2\nu_1 + \nu_3$
367.4	$\nu_{\text{asym}}(\text{CIPtCl})$	1820	$6\nu_1$
437.3	$\nu_1 + 131.5$	1925	$2\nu_1 + \nu_4$
512.0	$\nu_1 + 201.9$	2116	$7\nu_1$
524.0	$\nu_1 + 215.8$	2406	$8\nu_1$
574.4	$\nu_1 + 266.4$	2696	$9\nu_1$
602.2	$\nu_1 + \delta(\text{CIPtN})$	2986	$10\nu_1$
616.9	$2\nu_1$	3264	$11\nu_1$
677.6	$\nu_1 + \nu_{\text{asym}}$	3548	$12\nu_1$
742	$2\nu_1 + 131.5$	3828	$13\nu_1$
826	$2\nu_1 + 201.9/215.8$	4102	$14\nu_1$
923	$3\nu_1$	4372	$15\nu_1$
1040			

<sup>a</sup> etn  $\equiv$  ethylamine. <sup>b</sup> 514.5-nm excitation, KCl disk,  $\approx$  80 K.



**Figure 5.** Resonance Raman spectrum of the complex  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Br}_2]\text{Br}_4 \cdot 4\text{H}_2\text{O}$  recorded at ca. 80 K using 514.5-nm excitation. Spectral slit width  $\approx$  2  $\text{cm}^{-1}$ .

4). The wavenumbers of the band maxima are given in Table I. Single-crystal RR studies clearly showed that the fundamental band is polarized and therefore that all members of the  $\nu_1\nu_1$  progressions are totally symmetric.

The RR spectrum of RG at 80 K (Figure 5) likewise consists of an intense progression in  $\nu_1$  reaching as far as  $\nu_1 = 12$ , together with at least five subsidiary progressions, three of which are as follows:  $\nu(\text{CN}) + \nu_1\nu_1$  to  $\nu_1 = 4$ ,  $\delta(\text{HCH}) + \nu_1\nu_1$  to  $\nu_1 = 5$ ,  $\delta(\text{BrPtN}) + \nu_1\nu_1$  to  $\nu_1 = 7$  (Table II). These subsidiary progressions in the case of RG are more intense relative to the fundamental than is the case for those of WR.

The dominance in the RR spectrum by a progression in the axial breathing mode indicates that the principal effect of transferring an electron from the Pt(II) to the Pt(IV) constituent is that the Pt<sup>IV</sup>-X bond length increases (and that the Pt<sup>II</sup>...X bond length decreases). However, the appearance in the RR spectrum of bands attributable to  $\nu(\text{CN})$ ,  $\delta(\text{HCH})$ ,  $\delta(\text{NCH}_2)$ , and  $\delta(\text{XPtN})$  (X = Cl or Br) must also be accounted for. We believe that the appearance of these bands

**Table II.** Wavenumbers and Assignments of the Bands in the Resonance Raman Spectrum of the Complex  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Br}_2]\text{Br}_4 \cdot 4\text{H}_2\text{O}^a$ 

$\tilde{\nu}/\text{cm}^{-1}$	assignment	$\tilde{\nu}/\text{cm}^{-1}$	assignment
96.4	$\delta(\text{BrPtN}), \nu_2$	1054	$6\nu_1$
176.1 <sup>b</sup>	$\nu_{\text{sym}}(\text{BrPtBr}), \nu_1$	1082	$\nu(\text{CN}), \nu_3$
198.4		1150	$6\nu_1 + \nu_2$
220.9		1223	$7\nu_1$
230.3		1270	$\nu_1 + \nu_3$
260.7		1308	$\delta(\text{HCH}), \nu_4$
273.6	$\nu_1 + \nu_2$	1326	$7\nu_1 + \nu_2$
352.4	$2\nu_1$	1392	$8\nu_1$
401.6		1446	$2\nu_1 + \nu_3$
449.8	$2\nu_1 + \nu_2$	1484	$\nu_1 + \nu_4$
528.2	$3\nu_1$	1564	$9\nu_1$
580.7		1660	$2\nu_1 + \nu_4$
624.6	$3\nu_1 + \nu_2$	1747	$10\nu_1$
740.0	$4\nu_1$	1837	$3\nu_1 + \nu_4$
801	$4\nu_1 + \nu_2$	1917	$11\nu_1$
879	$5\nu_1$	2007	$4\nu_1 + \nu_4$
975	$5\nu_1 + \nu_2$	2177	$5\nu_1 + \nu_4$

<sup>a</sup> 514.5-nm excitation, KBr disk,  $\approx$  80 K. <sup>b</sup> This band is resolved into components at 175.9 and 180.1  $\text{cm}^{-1}$  at 0.5- $\text{cm}^{-1}$  resolution (see text).

can be explained in terms of a relief, in the excited state, of steric hindrance between the ethylamine groups and the axial halogen atoms. The detailed X-ray structure determination on RG shows (Figure 1) that the central platinum(IV) ion lies out of the plane of four coordinated nitrogen atoms by 11 pm, with  $\angle\text{Br-Pt-N} = 86^\circ$ .<sup>11,12</sup> This distortion from planar coordination for the nitrogen atoms was attributed to steric interactions between the methylene groups of the ligands and the axial halogen atoms, a proposal apparently confirmed by the fact that the Pt<sup>IV</sup>-Br bond nearest to the methylene group is slightly longer (by 3.2 pm) than that on the open side of the complex. Hence if anything relieves the steric interaction, the nitrogen atoms would be expected to adopt a more planar arrangement about the platinum(IV) ion. The mixed-valence transition can afford that relief since the platinum-halogen bond length is increased in the excited state, thus reducing the interaction. This reduction will lead to changes in the equilibrium position of several normal coordinates, e.g.,  $\delta(\text{NPtX})$ ,  $\delta(\text{NCH}_2)$ , and  $\delta(\text{HCH})$ , as the complex distorts on going from the ground to the excited state.

There is also a possibility that hydrogen bonding exists between the axial halogen and the hydrogen atoms of the methylene groups. If this is the case, any increase in the platinum-halogen bond length would tend to pull the hydrogen atoms in the same direction and hence lead to further distortion. These distortions affect coordinates which, according to the ideas of Tsuboi,<sup>13</sup> would then become involved in the RR spectrum. Only two bands are missing (or not readily assignable) that we might have expected if this explanation is correct: those arising from  $\delta(\text{PtNC})$  and  $\nu(\text{CH})$ . Both could, simply, be too weak to observe or else they might be obscured by other bands. Those bands that we have not assigned in Tables I and II are also probably due to deformation modes, but the assignments cannot readily be made.

**(b) Anhydrous Reihlen's Green and the Corresponding Iodide.** The isomorphous anhydrous bromo (ARG) and iodo (TSI) analogues of Wolfram's red and Reihlen's green also possess linear-chain, halogen-bridged structures. The essential features of their chains differ from those of the hydrated forms in that alternate PtN<sub>4</sub> units are staggered by 37° (Figure 1B) with respect to each other in the anhydrous complexes but eclipsed in the hydrated ones.<sup>6,12,14</sup> This structural difference has little if any consequence on the RR spectra (vide infra), as such spectra are determined almost solely by axial interactions.

The RR spectrum of ARG is virtually identical with that of RG, so it is not reproduced here. The value of  $\nu_1$  in ARG

Table III. Wavenumbers and Assignments of the Bands in the Resonance Raman Spectra of the Complexes  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{X}_2]\text{X}_4$ , X = Br or I

$\tilde{\nu}/\text{cm}^{-1}$		assignment
room temp	low temp	
	X = Br <sup>a</sup>	
96.2	101.0	$\delta(\text{NPtBr}), \nu_2$
181.6	181.3	$\nu_{\text{sym}}(\text{BrPtBr}), \nu_1$
216.1, 229.0	222.7	
278.5	282.9	$\nu_1 + \nu_2$
	336.0	
362.3	360.9	$2\nu_1$
404	404.9	$\nu_1 + 222.7$
454	463.1	$2\nu_1 + \nu_2$
	489.8	
543	539.3	$3\nu_1$
	584.8	$2\nu_1 + 222.7$
	620.5	
631	639.4	$3\nu_1 + \nu_2$
723	716.7	$4\nu_1$
	802	$\nu_1 + 620.5$
809		$4\nu_1 + \nu_2$
900	895	$5\nu_1$
	1073	$6\nu_1$
	1093	$\nu(\text{CN})$
	X = I <sup>b</sup>	
	112.9 sh	$\nu_a$
118.8	119.6	$\nu_{\text{sym}}(\text{IPtI}), \nu_1$
	128.6 sh	$\nu_b$
	231.6 sh	$\nu_1 + \nu_a$
237.0	239.5	$2\nu_1$
	251.7 sh	$\nu_1 + \nu_b$
	350.1 sh	$2\nu_1 + \nu_a$
355.3	357.7	$3\nu_1$
	371.8 sh	$2\nu_1 + \nu_b$
	474.1	$4\nu_1$
	591.9	$5\nu_1$
	611.0	
	624.8	
	(721)	$6\nu_1$
	731	$\nu_1 + 611.0$
	(836)	$7\nu_1$
	(957)	$8\nu_1$
	1290	
	1410	$\nu_1 + 1290.2$

<sup>a</sup> 488.0-nm excitation, KBr disk,  $\approx 80$  K. <sup>b</sup> 530.9-nm excitation, KI disk,  $\approx 80$  K.

(181.3  $\text{cm}^{-1}$ ) is slightly higher than that in RG (176.1  $\text{cm}^{-1}$ ), consistent with the fact that the platinum(IV)-bromine distances in the former (ca. 244 pm)<sup>6</sup> are less than in the latter (246.3 pm).<sup>12</sup>

The act of compressing, at  $\approx 9$  kbar, RG into a KBr disk was found to result in some of the compound being converted to ARG. This was shown by the fact that the  $\nu_1$  band in RG so compressed was a doublet under 0.5  $\text{cm}^{-1}$  resolution at ca. 80 K with  $\nu_1$  maxima at 175.9 and 180.1  $\text{cm}^{-1}$ . Therefore the irreversible phase change discovered by Interrante and Browall<sup>15</sup> when RG is subjected to a pressure of  $\approx 60$  kbar is probably the conversion of the hydrated to the anhydrous form of the compound.

The RR spectrum of the iodide, TSI, is similar to that of WR, RG, and ARG, in that the spectrum is dominated by a fairly long progression in the axial breathing mode,  $\nu_1$  ( $\text{IPt}^{\text{IV}}\text{I}$ ), reaching to  $\nu_1 = 8$ , together with two other two-membered progressions of the sort  $\nu_n + \nu_1$  (Figure 6). The enabling modes for these two progressions (at 611.0 and 1290.2  $\text{cm}^{-1}$ ) are possibly  $\nu(\text{PtN})$  and  $\delta(\text{HCH})$  modes, respectively. The band maxima are given in Table III.

(c) **Effects of Low Temperature.** The most striking effects of recording RR spectra of such mixed-valence compounds at low temperatures rather than at room temperature are the

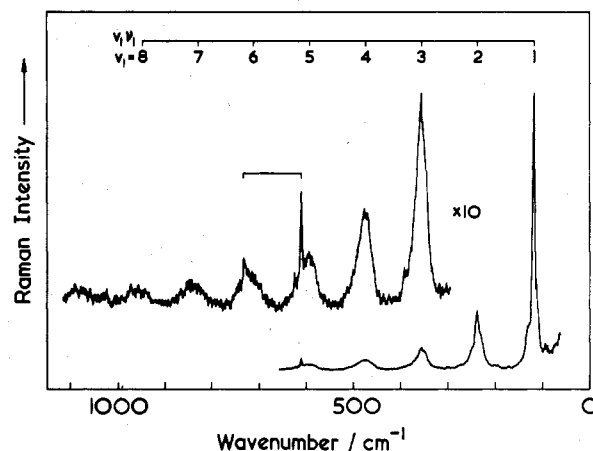


Figure 6. Resonance Raman spectrum of the complex  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{I}_4]$  recorded at ca. 80 K using 530.9-nm excitation. Spectral slit width  $\approx 2$   $\text{cm}^{-1}$ .

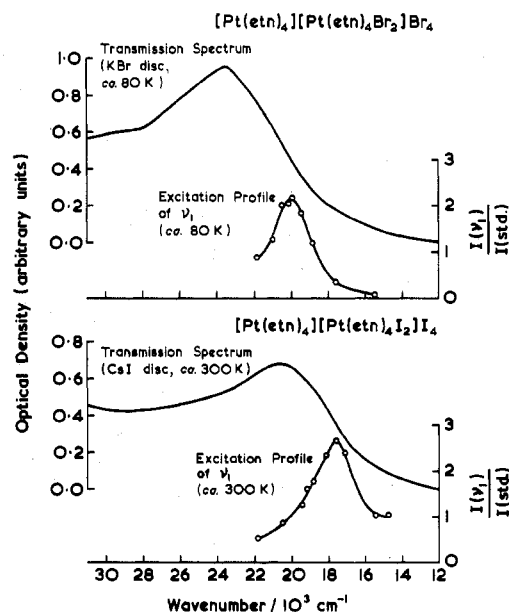


Figure 7. Electronic spectra (alkali halide disk) of  $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{X}_2]\text{X}_4$ , X = Br or I, together with the excitation profiles of the  $\nu_1, \nu_{\text{sym}}(\text{X}-\text{Pt}^{\text{IV}}-\text{X})$  band of each (181  $\text{cm}^{-1}$ , X = Br; 119  $\text{cm}^{-1}$ , X = I).

increase in the absolute intensity of the Raman bands and the increase in the intensities of overtone bands of  $\nu_1$  relative to that of the fundamental band. This increase in the absolute intensity of the fundamental band is by a factor of  $\approx 3$  (in peak height by a factor of 8–10) on changing from 300 to ca. 80 K. The increases in the intensities of the overtones are also striking, the first three overtone bands being all more intense than the fundamental band, whereas at 300 K the maximum value of even  $I(2\nu_1)/I(\nu_1)$  rarely exceeds 0.7 with any exciting lines.<sup>2</sup> These results are probably a consequence of there being more effective resonance between the frequencies of the laser beam and of the resonant electronic transition at low temperatures.

Another consequence of recording the RR spectra at ca. 80 K is that  $\nu_1$  of WR is reduced by  $\approx 8$   $\text{cm}^{-1}$  from its room temperature value; the value of  $x_{11}$  (vide infra) is also lower. The effect was not found for ARG or TSI. This may be a form of mode-softening,<sup>3</sup> but if so it is difficult to understand why all linear-chain compounds of this sort do not display the effect. Possibly WR undergoes a phase change between 300 and 80 K.

Table IV. Data Relating to the Electronic Spectra and the  $\nu_1$ -Band Excitation Profiles for the Mixed-Valence Complexes Studied

complex <sup>a</sup>	color		mixed-valence band maxima/cm <sup>-1</sup> DR <sup>c</sup>	excitation profile maxima/cm <sup>-1</sup> $\epsilon_{\parallel}$ <sup>d</sup>	excitation profile maxima/cm <sup>-1</sup>
	crystal (needles) <sup>b</sup>	powder			
WR	green-brown	orange-red	21 000	≈17 500	17 450
RG	green-gold	purple	18 250	≈16 500	15 950
ARG	orange	yellow	23 600	<i>e</i>	20 000
TSI	green-black	purple-brown	20 600	<i>e</i>	17 600

<sup>a</sup> WR = [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>4</sub>·4H<sub>2</sub>O, RG = [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>Br<sub>2</sub>]Br<sub>4</sub>·4H<sub>2</sub>O, ARG = [Pt(etn)<sub>4</sub>][Pt(etn)<sub>4</sub>Br<sub>2</sub>]Br<sub>4</sub>, TSI = [Pt(etn)<sub>4</sub>]-[Pt(etn)<sub>4</sub>I<sub>2</sub>][I<sub>4</sub>]. <sup>b</sup> By reflected light. <sup>c</sup> Diffuse reflectance results from ref 5. <sup>d</sup> Single crystal work, S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, 29, 894 (1956) (note that the captions to Figures 1 and 3 in the paper should be transposed). See also ref 3. <sup>e</sup> Not known.

(d) **Excitation Profiles.** The excitation profiles of  $\nu_1$  of WR,<sup>4</sup> RG,<sup>5</sup> ARG, and TSI (Figure 7) bear an unusual relation to the absorption spectrum. As can be seen from Figure 7 the maximum of the excitation profile of the Raman band does not coincide with the maximum of the mixed-valence charge-transfer absorption band. In the cases of WR<sup>3</sup> and RG<sup>5</sup> it has been found that there are apparently two mixed-valence transitions contributing to this band contour, and the RR excitation profile picks out only the one of lower energy. For ARG our low-temperature absorption spectrum did show a very weak shoulder at ≈19 500 cm<sup>-1</sup>—close to the maximum of the excitation profile—but since it was so ill-defined we cannot claim a definite correlation in this case (Table IV).

A definitive explanation of this phenomenon, and also of the (possibly related) effects which occur on dehydration of WR and RG, is still lacking. Any energy-level calculations on these systems would have to take into account (a) the bridging interaction between the halogen and the Pt(II) ions (resulting in a decrease in the frequency of  $\nu(\text{Pt-X})$  for the mixed-valence complex; cf. the isolated Pt(IV) complex) and (b) the presence of two Pt(IV) ions adjacent to each Pt(II) ion. The latter point seems to us to be significant in the light of changes that occur when RG is dehydrated. In the hydrated complexes each Pt(II) ion is approximately equidistant from the neighboring Pt(IV) ones and therefore the mixed-valence transition should be discussed in terms of a delocalization over two Pt(IV) centers rather than just one. For the anhydrous complexes the Pt(II) ion is appreciably closer to one Pt(IV) ion than to the other, and hence the mixed-valence transition is more likely to be localized on one Pt(IV) ion. This may be the reason why the mixed-valence transitions occur at a higher energy (Table IV) in ARG than in RG (TSI does not exist in a hydrated form and anhydrous WR has not, to our knowledge, been investigated spectroscopically, presumably because of its rapid rehydration in air). Why the chain structure should distort when the water molecules are removed is also a matter of speculation. Hydrogen bonding in the hydrated complexes is one obvious explanation. (The chain distortion occurring on dehydration resembles remarkably the Peierls distortion, occurring on cooling, in one-dimensional metals,<sup>1</sup> although we doubt that this is more than a coincidence.)

Although the anisotropic properties exhibited by this type of mixed-valence complex are not as important as those of compounds such as K<sub>2</sub>Pt(CN)<sub>4</sub>Br<sub>0.30</sub>·3H<sub>2</sub>O or (SN)<sub>x</sub>,<sup>1</sup> they seem to us to be worthy of further investigation, both experimental and theoretical.

**Vibrational Analysis.** The observation of a large number of overtones of a totally symmetric fundamental under RR conditions makes it possible to determine, by standard procedures, the harmonic frequency ( $\omega_1$ ) and anharmonicity constant ( $x_{11}$ ).<sup>16</sup> A plot of  $\nu_1\nu_i/\nu_1$  vs.  $\nu_1$  should be a straight line of gradient  $x_{11}$  and (to a first approximation) intercept  $\omega_1 + x_{11}$ . Such a plot is shown for the WR data in Figure 8; a particularly good straight-line relation is evident.

The results of such an analysis are summarized in Table V. In all cases, the band which displays the RR effect is close

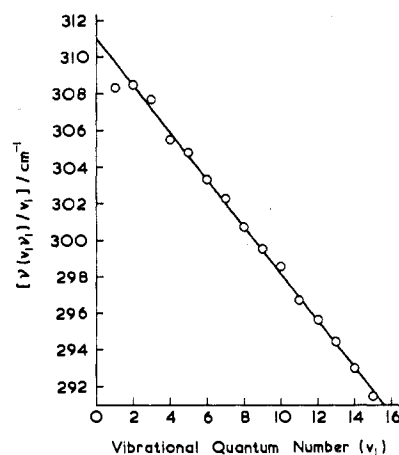


Figure 8. Plot of  $(\nu_1\nu_i)/\nu_1$  vs.  $\nu_1$  using the data derived from an RR study of Wolfram's red at ca. 80 K.

Table V. Harmonic Frequencies and Anharmonicity Constants at 300 and ca. 80 K for the Mixed-Valence Compounds Studied

Compd <sup>a</sup>	$\nu_1/\text{cm}^{-1}$		$\omega_1/\text{cm}^{-1}$		$x_{11}/\text{cm}^{-1}$ <sup>c</sup>	
	RT <sup>b</sup>	LT <sup>b</sup>	RT	LT	RT	LT
WR	316.6	308.3	319.5	312.3	-2.00	-1.29
RG	178.9	176.1	179.6	~177 <sup>d</sup>	-0.37	~-0.3
ARG	181.6	181.3	<i>e</i>	182.5	<i>e</i>	-0.65
TSI	118.8	119.6	<i>e</i>	120.3	<i>e</i>	-0.33

<sup>a</sup> For key to compound nomenclature, see footnote *a* to Table IV. <sup>b</sup> RT = room temperature, LT = liquid-nitrogen temperature. <sup>c</sup> Error in  $x_{11}$  is estimated to be  $\pm 0.04$  cm<sup>-1</sup>. <sup>d</sup> Not accurate, owing to pressure-induced partial conversion of RG into ARG in the disk. <sup>e</sup> Insufficient data to permit these quantities to be calculated.

to behaving as a simple harmonic oscillator, the average value of  $x_{11}/\omega_1$  being -0.0029 for the ca. 80 K data.

## Conclusion

The RR spectra of mixed-valence linear-chain halogen-bridged compounds are extremely intense, and such spectra can be used as criteria of whether or not a particular synthetic route has led to the formation of this type of compound.

The coordinate mainly affected by the mixed-valence transition is  $\nu_1$ , the symmetric X-Pt<sup>IV</sup>-X stretching mode, whose excitation profile maximizes close to the maximum of the lower mixed-valence transition. Other coordinates affected to a much lesser extent involve slight changes in the orientation of the Pt(etn)<sub>4</sub> groups with respect to the chain direction consequent upon a lengthening of the Pt-X bonds in the resonant excited state. These conclusions are consistent with those of Tsuboi<sup>13</sup> on the theory of the RR effect, in that coordinates involved in converting the molecule from its ground- to its (resonant) excited-state geometry are those which suffer most resonance enhancement.

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**Registry No.** WR, 50600-57-2; RG, 58559-78-7; ARG, 12081-56-0; TSI, 60428-74-2.

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## Metal Complexes of Cyclic Triamines. 2. Stability and Electronic Spectra of Nickel(II), Copper(II), and Zinc(II) Complexes Containing Nine- through Twelve-Membered Cyclic Triamine Ligands

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The acidity constants of three cyclic triamines, 1,4,7-triazacyclodecane ([10]aneN<sub>3</sub>), 1,4,8-triazacycloundecane ([11]aneN<sub>3</sub>), and 1,5,9-triazacyclododecane ([12]aneN<sub>3</sub>), were measured at 25 °C in aqueous 0.1 F KNO<sub>3</sub>. The formation constants of each of these amines with Ni(II), Cu(II), and Zn(II) were obtained as well as the hydrolysis equilibrium constants for several of the complexes. The results indicate that these complexes are generally more stable than those with the corresponding linear or branched triamine ligands. The stability of the cyclic triamines varies inversely with ligand ring size. The electronic spectra of Ni[x]aneN<sub>3</sub><sup>2+</sup> (x = 9, 10, 11, 12) are presented and trends in the ligand field parameter (*Dq*) and nephelauxetic ratio ( $\beta$ ) for these complexes are discussed. The compounds [Ni[12]aneN<sub>3</sub>(OH)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> and [Cu([11]aneN<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O were synthesized and isolated. Electronic and infrared spectra are presented along with magnetic susceptibility data.

### Introduction

The series of cyclic triamines shown in Figure 1 presents a nearly ideal system to study the properties of metal complexes which contain ligands with similar coordinative tendencies yet which progressively distort the stereochemical environment of the metal. Although the synthesis of [12]-aneN<sub>3</sub> was published in 1966,<sup>1</sup> few studies of metal complexes containing cyclic triamines were reported prior to 1972.<sup>2</sup> Since that time, several investigations of metal complexes of cyclic triamines have appeared in the literature<sup>3-12</sup> and it is likely that interest in these and similar cyclic compounds where one or more nitrogens are replaced by other heteroatoms will continue to grow.

The extra stability of [9]aneN<sub>3</sub> complexes has been well documented<sup>4-6</sup> and our preliminary work<sup>5</sup> with the remaining congeners suggested that these cyclic amines behave similarly. In this work the preliminary study has been refined and considerably extended, and we show that this entire series of cyclic amines forms complexes which are generally several orders of magnitude more stable than those which contain corresponding linear and branched triamines. Trends in acid dissociation among the ligands as well as complex stability in relation to ligand ring size are also presented and discussed.

Another interesting aspect of cyclic triamine chemistry is the spectroscopic behavior of the complexes. In particular, the bis nickel(II) complexes show a wide range of values for the ligand field parameter (*Dq*). As with the macrocyclic complexes of saturated tetraamines,<sup>13</sup> those complexes con-

taining the smaller ring ligands have the largest values of *Dq*. On the basis of an octahedral model, the values of *Dq* for Ni([9]aneN<sub>3</sub>)<sub>2</sub><sup>2+</sup> and Ni([10]aneN<sub>3</sub>)<sub>2</sub><sup>2+</sup> are among the largest reported for any alkylamines.<sup>6,7</sup> We now report the electronic spectra of the mono nickel(II) complexes of the triamines. Both *Dq* and  $\beta$  (the nephelauxetic ratio) are calculated for these complexes and based upon these values certain aspects of their structure and bonding are discussed.

The synthesis and characterization of two new complexes, [Ni[12]aneN<sub>3</sub>(OH)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> and [Cu([11]aneN<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O are also described.

### Experimental Section

**Materials.** All reagents and solvents used were reagent grade and were used without further purification. Solutions of nickel(II), copper(II), and zinc(II) as the nitrates were standardized by complexometric techniques.<sup>14</sup> The cyclic triamines were all synthesized using Richmann's modification<sup>15</sup> of the method of Koyama and Yoshino.<sup>3</sup> The trihydrochloride salts of the amines were prepared in nearly quantitative yield from the trihydrobromide salts.<sup>6</sup> Analyses, NMR spectral data, and melting points of these salts are given in Table I.

**Metal Complexes.** The complexes of [9]aneN<sub>3</sub> and [10]aneN<sub>3</sub> were prepared as the nitrate and/or perchlorate salts by methods previously described.<sup>6,7</sup>

**[Cu([11]aneN<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O.** To an ethanolic (15 mL) slurry of 120 mg of [11]aneN<sub>3</sub>·3HCl (0.450 mmol) was added 76 mg of KOH (1.4 mmol), and the solution was then heated at 60 °C for 15–20 min. After being cooled, the solution was filtered into 10 mL of an ethanolic solution containing 54.4 mg of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.225 mmol). Blue