gen in the slow step. A rapid reoxidation to give products is then visualized. Such a process may well be operative here for palladium(IV), since it is observed with the bromide entering ligand which would be more easily oxidized by Cl^+ than an entering chloride by Br^+ for example.

Reaction 2 exhibits a first-order term in the rate law eq 6, indicating a reaction path with a slow step independent of entering chloride and $Pd(en)_2^{2+}$. It is reasonable, though admittedly speculative, to ascribe this first-order path to a dissociative or dissociative interchange process of the reactive *trans*-$Pd(en)_2Br_2^{2+}$ substrate. In support of this suggestion, the entropy of activation is more positive (though still negative) than ΔS^* observed for the catalyzed path. The Pd^{IV}–Br bond is expected to be more easily ruptured in a purely dissociative process than Pd^{IV}–Cl since the bond energies are likely to be in the order $Pd^{IV}\text{–}Cl > Pd^{IV}\text{–}Br$ as for platinum(IV). Thus, for the *trans*-$Pd(en)_2Br_2^{2+}$ cation, this pathway can compete effectively with the catalyzed path.

Finally, the observed changes in the spectra of *trans*-$Pd(en)_2Br_2^{2+}$ as a function of bromide ion concentration are ascribed to ion-pair formation, eq 4. Accompanying the increase in absorptivity as the bromide concentration is raised, there is also a notable blue shift to 37,700 cm^{-1} of the charge-transfer band at 34,700 cm^{-1} in *trans*-$Pd(en)_2Br_2^{2+}$. This shift of the charge-transfer band, which is presumably ligand to metal in character, is consistent with a reductive interaction between bromide and the complex cation. Partial reduction of palladium(IV) will reduce the positive charge on the metal and therefore destabilize metal acceptor orbitals causing a blue shift for the ligand to metal charge-transfer band. A reasonable suggestion as to the structure of the ion pair might be

$$[Br\text{–}Pd(en)_2\text{–}Br\cdot\cdot\cdot Br]^+$$

It is worth noting that the association constants K for the numerous platinum(IV) complexes which exhibit similar behavior must be appreciably smaller than the value of $20 \pm 2\,M^{-1}$ estimated here for *trans*-$Pd(en)_2Br_2^{2+}$, since no evidence of limiting absorbance values has been found.

Registry No. Bis(ethylenediamine)palladium(II) chloride, 16483-18-4; *trans*-dichlorobis(ethylenediamine)palladium(IV) bis(ethylenediamine)palladium(II) nitrate, 9076-08-8; *trans*-$[Pd(en)_2Cl_2Pd(en)_2][ClO_4]_4$, 9047-90-9; *trans*-$[Pd(en)_2Cl_2][ClO_4]_2$, 36245-59-7; *trans*-$[Pd(en)_2Br_2Pd(en)_2][ClO_4]_4$, 9076-07-7; *trans*-$[Pd(en)_2Br_2]Br_2\cdot 2HBr$, 36223-03-7; Br^-, 24959-67-9; Cl^-, 16887-00-6.

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Contribution from Ames Laboratory and the Chemistry Department,
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Polarized Crystal Spectra of Yellow Cossa's Salt, Potassium Trichloroammineplatinate(II) Monohydrate, and Red Cossa's Salt

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Evidence is provided that the yellow Cossa's salt is $KPt(NH_3)Cl_3\cdot H_2O$. The red Cossa's salt apparently contains small quantities of the octahedral ions of platinum(IV), $Pt(NH_3)Cl_5^-$, which replace the planar ions in the crystals. Crystal spectra for the yellow salt at 300 and 15°K are reported, and the transition assignments are discussed in terms of selection rules for ligand field and vibronic excitations. The temperature dependence of spectra for a red crystal indicate a dipole-allowed transition with its polarization in the stacking direction at 23,800 cm^{-1}. The new compound $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5]\cdot 2H_2O$ is reported which has alternately stacked planar Pt^{II} and octahedral Pt^{IV} complex anions and a very high absorption for polarization in the stacking direction. It is proposed that the band at 23,800 cm^{-1} in the red crystal constitutes a mixed-valence electron-transfer transition.

Introduction

Polarized crystal spectra in the d ← d region of K_2PtCl_4 have indicated that the absorption of the $PtCl_4^{2-}$ ion in the crystal resembles very closely its solution spectrum.[1] The $PtCl_4^{2-}$ ion occupies a position of full D_{4h} symmetry in the crystal, and the ions stack along the c axis of the tetragonal crystal with 4.14-Å separations.[2] With its center of symmetry the d ← d transitions are forbidden and can presumably occur only by means of a vibronic mechanism whereby an asymmetric vibration serves as a perturbation which mixes in asymmetric wave functions. According to the vibronic selection rules for $PtCl_4^{2-}$, the transition $^1A_{2g} \leftarrow {}^1A_{1g}$ ($d_{x^2-y^2} \leftarrow d_{xy}$) is forbidden in z-c polarization and can therefore be unequivocally identified in the polarized crystal spectra. In addition, the spectra at low temperatures confirmed the vibronic model since the absorption intensities were strongly reduced. The better resolution at liquid helium temperatures revealed two additional absorption bands.

Recently, polarized spectra for the molecular crystals of dichloro(ethylenediamine)platinum(II) were reported.[3] These nearly planar molecules do not possess a center of symmetry. Therefore, many transitions may contain a nonzero transition dipole, and selection rules must be based upon the symmetry of the molecule or the "ligand fields." However, these molecules stack with separations of only 3.39 Å and the intermolecular interactions introduce major modifications into the spectra. Indeed, certain absorption

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(1) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 4, 1682 (1965).

(2) (a) E. Staritzky, *Anal. Chem.*, 28, 915 (1956); (b) R. H. Mais, P. G. Owston, and A. M. Wood, *Acta Crystallogr., Sect. B*, 28, 393 (1972).

(3) D. S. Martin, Jr., L. D. Hunter, R. Kroening, and R. F. Coley, *J. Amer. Chem. Soc.*, 93, 5433 (1971).

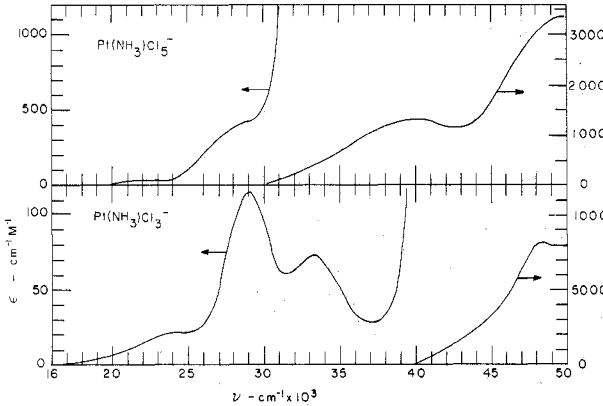

Figure 1. Spectra of solutions of the $Pt(NH_3)Cl_3^-$ and $Pt(NH_3)Cl_5^-$ ions.

bands have been attributed to excited ionic crystal states. The crystal structure of $KPt(NH_3)Cl_3 \cdot H_2O$, reported by Jeannin and Russell,[4] indicates that the planar $Pt(NH_3)Cl_3^-$ anions are stacked with a separation of 4.57 Å. The present work was undertaken since the crystals appeared to provide an example where "ligand field" excitations should occur but for which interionic effects would be a minor factor.

Experimental Section

Materials. $KPt(NH_3)Cl_3 \cdot H_2O$, *Cossa's salt*, was prepared by the method of Elleman, *et al.*,[5] and the ultraviolet solution spectrum agreed with that reported by them.

The removal of any $PtCl_4^{2-}$ in solutions of the preparation by additions of $Pt(NH_3)_4^{2+}$ to give the exceedingly insoluble Magnus' green salt, $Pt(NH_3)_4PtCl_4$, was monitored by observing the ultraviolet spectrum of the solutions. The final purification was accomplished by visually selecting only large "yellow" plates to make up the final crystallizing solution. Most difficulties encountered in the preparation of this compound result from its astonishingly high solubility in water. Crystals suitable for spectroscopy could be removed from a crystallizing liquor by a curved platinum spatula. Jorgensen[6] reported that the compound crystallizes in both "red" and "yellow" forms. Evidence is presented below that the "yellow" crystals constitute the pure compound.

$KPt(NH_3)Cl_5 \cdot H_2O$ was prepared by bubbling chlorine gas through a saturated aqueous solution of $KPt(NH_3)Cl_3$. The bright yellow product is rather insoluble and precipitates out during the process. It was recrystallized from water. It was analyzed by careful reduction with SO_2 and observation of the spectrum of $Pt(NH_3)Cl_3^-$.

$K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5] \cdot 2H_2O$ was prepared by mixing 1:1 molar quantities of $KPt(NH_3)Cl_3$ and $KPt(NH_3)Cl_5$ in an aqueous solution. Crystals were obtained upon evaporation. The lustrous orange crystals were selected by hand from minor amounts of the component compounds. A specimen was analyzed by thermogravimetric means with the following results: 110–135°: wt loss, 4.1; calcd for H_2O, 4.4; 290–550°: wt loss, 28.2; calcd for NH_3 + 3Cl, 30.0; 780–945°: wt loss, 18.1; calcd for KCl, 18.4; residue, 50.0; calcd for Pt, 47.5. The low chloride and high platinum analyses suggest some contamination with the platinum(II) component.

"Red" $KPt(NH_3)Cl_3$ was cut from the ends of large crystals which contained both red and yellow sections. These sections were dissolved in KCl solutions for the measurement of their absorption spectra in an aqueous medium. A crystal suitable for spectroscopy was obtained by chance from a solution which was crystallized in a film of solution between two polished silica plates. A drop of solution was placed on one plate and a second plate placed over it. The crystals formed as the water evaporated from the edges of the film.

Procedures. Spectra for aqueous solutions were measured with a Cary spectrophotometer, Model 14. Glan type polarizers were inserted into the reference and sample beams of the spectrophotometer. Crystals were mounted over pinholes from 0.5 to 1 mm in diameter in platinum plates. A similar pinhole and sometimes screens were placed in the reference beam. For low-temperature studies the platinum pinhole plates were mounted against a copper block which served as the bottom of a cryostat which could contain liquid nitrogen or helium. With liquid helium a nominal temperature of 15°K has been assumed for the samples. The samples were attached to the pinhole plates by a drop of electrical varnish.

For low-temperature work, the design of the cryostat required that the crystals be maintained under vacuum. Prolonged exposure to vacuum at room temperature results in a disintegration of the crystal which accompanies the loss of the crystal water. Therefore, as soon as the cryostat was pumped out, liquid nitrogen was introduced. At such low temperature the crystals survived for the period required for spectral measurements; however, the crystals were always lost upon rewarming to room temperature.

With a crystal mounted in the beam, the polarizers were rotated at a suitable wavelength to find the maximum and minimum absorbances. A reference line was obtained with pinholes in both the reference beam and the sample beam. Absorbances were considered to be zero at 600 nm. Crystals with measured area were weighed by a Cahn electromicrobalance. Since the thickness could be inferred from these measurements and the concentration is available from the crystal structure density, the absorbances were converted to molar absorptivities. The spectra were resolved into the recorded bands by a least-squares fitting program provided by Siano and Metzler.[7] Although this program provided for skewed bands, all the fitted bands were within 2% of gaussians.

Thermogravimetric analyses were performed by means of a Du Pont 950 thermogravimetric analyzer in which the samples were heated 5°/min in a stream of dry nitrogen.

Results and Discussion

Solution Spectrum of $Pt(NH_3)Cl_3^-$. The solution spectrum for an aqueous solution of $Pt(NH_3)Cl_3^-$ is presented in Figure 1. The low-energy region, $< 40{,}000$ cm^{-1}, was recorded promptly upon dissolving the potassium salt in a 0.1 *M* KCl solution which was added to suppress aquation. However, the high-energy portion was recorded for a dilute aqueous solution as rapidly as possible following dissolution of the salt to avoid absorption by free chloride. The spectrum is essentially in agreement with that reported by Chatt, Gamlen, and Orgel.[8] The energies of the maxima for the resolved bands, their intensities, and proposed assignments have been given in Table I. The fitting program was not sufficiently sensitive to resolve the lowest energy band which was fitted by hand. Otherwise, the $\bar{\nu}$ and ϵ were taken from the fitted components and the oscillator strengths were calculated from the expression

$$f = 4.60 \times 10^{-9} \epsilon_{\max} \bar{\nu}_{1/2} \qquad (1)$$

where $\bar{\nu}_{1/2}$ is the half-width of the band. The spectrum has the typical features of the spectra of the chloroammine complexes of platinum(II). These spectra are discussed in terms of the relative ordering of orbitals involved in the spectroscopically accessible electronic transitions for $Pt(NH_3)Cl_3^-$ presented in Figure 2. The free $Pt(NH_3)Cl_3^-$ ion possesses a C_{2v} local symmetry at the platinum atom, and the symmetries of the d orbitals are shown in Figure 2 in both D_{4h} and C_{2v}. For C_{2v}, an unconventional set of axes has been chosen in that the *z* axis is retained normal to the plane of the ion. The nitrogen of the ammonia and its trans chloride are placed on the *y* axis, which serves as the C_2 axis, and the other two chlorides are placed along the *x* axis. Table II provides the C_{2v} character table utilized for

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[4] Y. P. Jeannin and D. R. Russell, *Inorg. Chem.*, **9**, 778 (1970).

[5] T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Amer. Chem. Soc.*, **80**, 536 (1958).

[6] S. M. Jorgensen, *Z. Anorg. Chem.*, **24**, 153 (1900).

[7] D. B. Siano and D. E. Metzler, *J. Chem. Phys.*, **51**, 1856 (1969).

[8] J. Chatt, G. O. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

Table I. Aqueous Solution Spectrum for $Pt(NH_3)Cl_3^-$

Energy, $\bar{\nu}$, cm^{-1}	Molar absorp, ϵ, $cm^{-1}\ M^{-1}$	Oscillator strength, $10^4 f$	Transition assignment, ground state $^1A_1$	Ligand field polarizn	Vibronic polarizn
20,800	(6)	(1.60)	$^3B_2\ (\sigma^* \leftarrow d_{xy})$		
24,000	20.5	5.3	$^3A_2\ (\sigma^* \leftarrow d_{xz})$ $^3B_1\ (\sigma^* \leftarrow d_{yz})$		
28,900	109	16	$^1B_2\ (\sigma^* \leftarrow d_{xy})$	x	x, y
33,400	71	16	$^1A_2\ (\sigma^* \leftarrow d_{xz})$ $^1B_1\ (\sigma^* \leftarrow d_{yz})$	Forbidden z	x, z y, z
Not obsd			$^1A_1\ (\sigma^* \leftarrow d_{z^2})$	y	y, z, x
45,300 48,100	2500 5900	640 870	$^1A_1{}^1B_1{}^1B_2\ (\sigma^* \leftarrow Cl\ \pi)$	Dipole-allowed y, z, x	

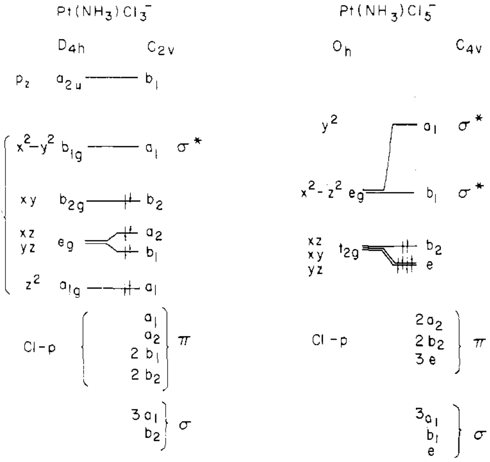

Figure 2. Relative ordering of the orbitals for the $Pt(NH_3)Cl_3^-$ and $Pt(NH_3)Cl_5^-$ ions.

the symmetry assignments. The lowest unfilled orbital is an antibonding σ^* based primarily on a $d_{x^2-y^2}$ orbital with symmetry a_1. The a_1 symmetry of the d_{z^2} orbital indicates that some d_{z^2} will be mixed in with the σ^* orbital as well.

In the $Pt(NH_3)Cl_3^-$ spectrum it is seen that there are at low energies two weak bands which can be assigned as spin-forbidden $\sigma^* \leftarrow d$ and then at somewhat higher energies two spin-allowed $\sigma^* \leftarrow d$ bands. The assignments of these $\sigma^* \leftarrow d$ transitions are those of Chatt, *et al.*[8] The ordering of the d orbitals corresponds to that for $PtCl_4^{2-}$, which has been confirmed by crystal spectra[1] and by magnetic circular dichroism.[9,10] The degeneracy of the e_g orbitals of D_{4h} has, of course, been broken in the C_{2v} symmetry. Chatt, *et al.*,[8] who did not resolve a second high-intensity band assigned the intense absorption to 6p ← 5d. However, polarized crystal spectra of dichloro(ethylenediamine)platinum(II) have provided evidence for an intermolecular transfer of chloride π electrons into the antibonding σ orbitals to give excited ionic exciton states.[3] Therefore, an assignment of these bands as $\sigma^* \leftarrow Cl\ \pi$ appears more likely. The energy shift of the $\sigma^* \leftarrow d$ bands and $\sigma^* \leftarrow Cl\ \pi$ bands to higher energies when one of the chlorides of $PtCl_4^{2-}$ is replaced by NH_3 is evident from Table I. This shift is consistent with the spectrochemical series of Fajans[11] and Tsuchida.[12]

The ion $Pt(NH_3)Cl_3^-$ does not possess a center of symmetry, and the $\sigma^* \leftarrow d$ transitions may have a nonzero transition dipole moment. The occurrence of such nonzero transition moments is sometimes called "ligand field excitation." Such nonzero transition moments can be inferred from the properties of the irreducible representations of the C_{2v} symmetry group. Thus, in a spin-allowed transition, if an electron is excited from an orbital u^0 to the u' orbital, the transition dipole moment for $u' \leftarrow u^0$ will contain the integral

$$\mu = \int u^{0*} \mid \mathbf{r} \mid u' \, d\tau \qquad (2)$$

where $\mathbf{r}$ is the vector representing the coordinates of the electron. For a nonzero integral, it is required that $u^0u' = B_2$ for x polarization, A_1 for y polarization, and B_1 for z polarization. The polarization for the ligand field excitations of the transitions for $Pt(NH_3)Cl_3^-$ are included in Table I. It is seen from this table that in the solution spectrum the band with a maximum at 28,900 cm^{-1} is assigned to the transition $^1B_2 \leftarrow {}^1A_1\ (\sigma^* \leftarrow d_{xy})$, for which the x component of the transition moment may be nonzero. The observed molar absorptivity for that band is 109 $cm^{-1}\ M^{-1}$ whereas for the corresponding transition[1] in $PtCl_4^{2-}$ it is 57 $cm^{-1}\ M^{-1}$. Hence, from the increased intensity it can be inferred that the ligand field excitation for this transition in $Pt(NH_3)Cl_3^-$ is of the same magnitude as the vibronic contribution.

Table II. Character Table for C_{2v} with the Choice of Axes

	E	C_2	σ	σ'	
A_1	1	1	1	1	z^2, x^2, y^2, y
A_2	1	1	−1	−1	xz
B_1	1	−1	1	−1	z, yz
B_2	1	−1	−1	1	x, xy

For the vibronic excitations the platinum and the four adjacent atoms are considered to constitute the vibrating entity. This approximation is probably satisfactory since frequencies involving the N-H bonds will be higher than those of the Pt-Cl bonds. The five-atom system possesses 9 vibrations, and the standard methods of group theory classify these as 4 A_1, 2 B_1, and 3 B_2 under the C_{2v} symmetry. The vibronic selection rules require that

$$\begin{aligned} u^0 Q_i u' &= B_2 \quad (x \text{ polarization}) \\ &= A_1 \quad (y \text{ polarization}) \\ &= B_1 \quad (z \text{ polarization}) \end{aligned} \qquad (3)$$

where Q_i is the normal vibration coordinate. For example, for the first spin-allowed transition, $^1B_2 \leftarrow {}^1A_1\ (a_1 \leftarrow b_2)$, the possible vibronic polarizations are x and y. The indicated vibronic polarizations for the spin-allowed $\sigma^* \leftarrow d$ transitions are included in Table I.

Crystal Spectra of $KPt(NH_3)Cl_3 \cdot H_2O$. A unit cell for the crystal of the "yellow" $KPt(NH_3)Cl_3 \cdot H_2O$ in the structure reported by Jeannin and Russell[4] is shown in Figure 3. In their study they concluded that there was a disorder in the potassium and water positions. The C_{2v} symmetry for the ion was not required by the crystal symmetry. Deviations from C_{2v} for the ion configuration however did not appear to be greater than the experimental error. The crystal lattice was *c*-centered orthorhombic with 4 formula weights

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(9) D. S. Martin, J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 5, 491 (1966).

(10) A. F. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Amer. Chem. Soc.*, 90, 5730 (1968).

(11) K. Fajans, *Naturwissenschaften*, 11, 165 (1923).

(12) R. Tsuchida, *Bull. Chem. Soc. Jap.*, 13, 388, 436 (1938).

Table III. Absorption Bands Resolved from Polarized Crystal Spectra of $KPt(NH_3)Cl_3 \cdot H_2O$ and Their Transition Assignments[a]

$\bar{\nu}_{max}$, cm^{-1}		Molar absorp, ϵ, $cm^{-1} M^{-1}$		Oscillator strength × 10^4		Transition assignment, ground state $^1A_1$
c-x	a-z	c-x	a-z	c-x	a-z	
20,000		22		3.3		$^3B_2$ ($\sigma^* \leftarrow d_{xy}$)
(20,200)		(27)		(4.9)		
23,300	24,300	41	11	6.6	2.8	$^3A_2$, $^3B_1$ ($\sigma^* \leftarrow d_{xz,yz}$)
(23,300)	(23,900)	(52)	(23)	(11)	(4.9)	
29,400		334		44		$^1B_2$ ($\sigma^* \leftarrow d_{xy}$)
(28,800)		(303)		(45)		
	29,200		10		0.9	$^3A_1$ ($\sigma^* \leftarrow d_{z^2}$)
	(28,700)		(15)		(2)	
32,500		47		11.3		$^1A_2$ ($\sigma^* \leftarrow d_{xz}$)
(32,100)		(108)		(28)		
	33,700		59		11	$^1B_1$ ($\sigma^* \leftarrow d_{yz}$)
	(33,000)		(106)		(19)	

[a] Values without parentheses are for liquid helium temperature (15°K) and those in parentheses are for 300°K.

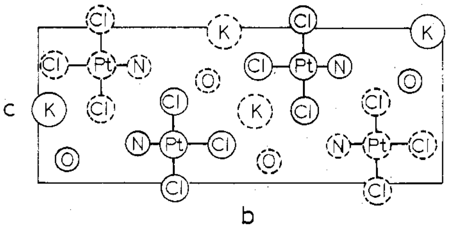

Figure 3. Unit cell for $KPt(NH_3)Cl_3 \cdot H_2O$. Solid atoms at $x = 0$, Dashed atoms at $x = 1/2$.

per unit cell. The square-planar ions stacked one directly above another along the *a* axis. The 4.57-Å stacking distance is somewhat greater than that between the platinum atoms in K_2PtCl_4. The symmetry axis of each ion was along the *b* crystallographic axis. Kukina and Bokii[13] in an earlier structure determination agreed with the placing of the platinum complexes but placed potassium ions and waters somewhat differently. They reported one major difference in their diffraction data from that of Jeannin and Russell, *viz.*, a superlattice which required a tripling of the *a* axis. However, in the solution of their structure they included only diffraction spots with *h* divisible by 3, and therefore the data set agreed well with that of Jeannin and Russell. In the present work a superlattice with a tripling of the *a* axis has been observed for "red" crystals, and it is suspected that Kukina and Bokii may have had a "red" crystal.

Crystals were grown from a saturated aqueous solution of $KPt(NH_3)Cl_3 \cdot H_2O$, they were thin plates with well-developed 010 faces. Thus light could be directed through the crystal by a beam which was parallel to the symmetry axis of the complexes. It is possible to record the absorption for polarized light with the electric vector directed along the *a* crystallographic axis, *i.e.*, the *z* molecular axis or along the crystallographic *c* axis or the *x* molecular axis. The spectra recorded for a crystal in both these polarizations at room temperature and helium temperatures are shown in Figure 4. The bands resolved from the crystal spectra together with the proposed assignment are presented in Table III.

These crystal spectra are completely consistent with the packing of complex ions of C_{2v} symmetry and the transition assignments of Table I into a crystal for which there are only very small crystal perturbations. For example, the maximum absorption in the $\sigma^* \leftarrow d$ region for the solution is at 28,900 cm^{-1}. In the crystal the strongest absorption in this region is at 28,800 cm^{-1} at 300°K in *c* or *x* polarization with only a barely discernible absorption at 28,700 cm^{-1} in *a* or *z* polarization. It is noted that the

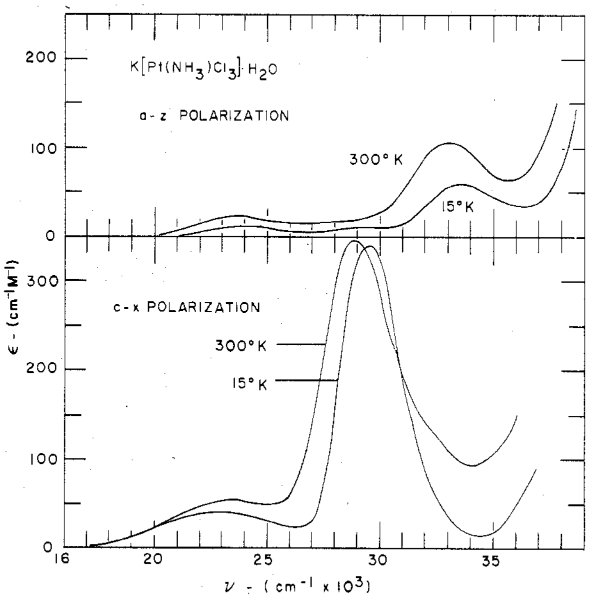

Figure 4. Polarized crystal spectra for $KPt(NH_3)Cl_3 \cdot H_2O$ (yellow crystals).

assigned transition $^1B_2 \leftarrow {}^1A_1$ has both a ligand field and vibronic excitation with *x* polarization but is completely forbidden in *z* polarization. A vibronic excitation is expected to decrease in width and height as the crystal is cooled whereas a transition with a transition dipole is expected to heighten as it narrows at low temperatures.[14] The fact that the height of this band scarcely changes upon cooling to 15°K indicates that the contribution of the ligand field and vibronic excitation very nearly balance.

There is a weak absorption in *a-z* polarization at the energy of 28,700-29,000 cm^{-1}. Since in exact C_{2v} symmetry the $^1B_2 \leftarrow {}^1A_1$ transition is forbidden in this polarization, the very weak absorption may result from a breaking of the C_{2v} symmetry by a lower crystal site symmetry. However, the crystal spectrum of K_2PtCl_4 indicates a weak spin-forbidden transition $d_{x^2-y^2} \leftarrow d_{z^2}$ in the vicinity of the $d_{x^2-y^2} \leftarrow d_{xy}$ spin-allowed transition. Therefore, the assignment as $^3A_1 \leftarrow {}^1A_1$ for the absorption in *a-z* polarization at 28,700 cm^{-1} is tentatively proposed.

The major peak in *a-z* polarization for the crystal at 33,000 cm^{-1} is assigned to the spin-allowed $^1B_1 \leftarrow {}^1A_1$ ($\sigma^* \leftarrow d_{yz}$). From symmetry, the transition should be allowed by ligand field excitation. However, it has a low intensity and a high ratio of 1.8 in oscillator strength

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[13] G. A. Kukina and G. B. Bokii, *Zh. Strukt. Khim.*, 6, 233 (1965).

[14] W. R. Mason, III, and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 5722 (1968).

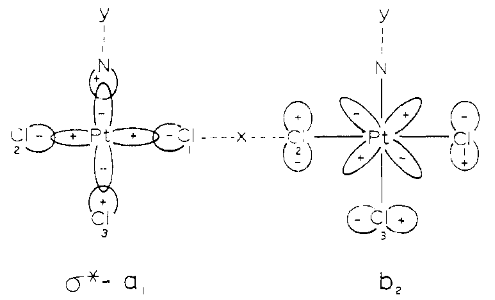

Figure 5. Principal atomic orbital components in σ^*-a_1, the lowest unfilled orbital, and in the highest filled orbital, b_2.

between 300 and 15°K, in comparison to the band in *c-x* polarization at 28,800 cm^{-1}. Such behavior indicates a relatively low "ligand field" transition moment and that most of the excitation is by the vibronic mechanism.

It is interesting to speculate on the apparent difference in the "ligand field" transition moments of these two transitions, *viz.*, the $^1B_2 \leftarrow {}^1A_1$ ($\sigma^* \leftarrow d_{xy}$) at 28,800 cm^{-1} with the high transition moment in the *x* polarization and the $^1B_1 \leftarrow {}^1A_1$ ($\sigma^* \leftarrow d_{yz}$) at 33,000 with the low transition moment in the *z* polarization. The major components of the LCAO for σ^*, *viz.*, $d_{x^2-y^2}$ and the ligand σ orbitals, are shown in the sketch of Figure 5. It should be noted that symmetry would also permit the mixing of some ligand π orbitals ($\pi_{y_1} + \pi_{y_2}$) which would presumably be a very minor component because of their zero overlap with the $d_{x^2-y^2}$. The MO may also include the minor component of d_{z^2} as well as the p_y orbitals of the platinum which have a_1 symmetry. If the b_2 orbital were pure d_{xy}, a nonzero overlap would result for the following components of μ_x

$$\mu_x = \int d_{xy} |x| (C_1\sigma_N + C_2\sigma_2)\, d\tau + \int d_{xy} |x| C_3 p_y\, d\tau + \cdots \quad (4)$$

The first integral in eq 4 could be nonzero because of the difference in overlap with the nitrogen and chloride σ orbitals. However, the transition moment μ_z for the transition $^1B_1 \leftarrow {}^1A_1$ must contain exactly equivalent terms; and, accordingly, it is concluded that the two integrals in eq 4 likely contribute moments of opposite sign which largely cancel each other.

However, the b_2 orbital contains other components besides d_{xy}. It is recognized as having some π-antibonding character and the ligand π orbitals which interact with d_{xy} are shown in Figure 5 also. In addition to these, there will be the minor σ components ($\sigma_1 - \sigma_2$). Also the p_x orbital overlaps not only with this σ orbital but also with the π_{x_3} as well. Therefore, in addition to the terms in eq 4 the additional component of μ_x (eq 5) must be considered. The integral will be large because $d_{x^2-y^2}$ has

$$\mu_x = \cdots + C_x C_{x^2-y^2} \int p_x |x| d_{x^2-y^2}\, d\tau + \cdots \quad (5)$$

a large σ component along the *x* axis, and this integral represents effectively a $\sigma_g \leftarrow \sigma_u$ transition. The b_1 orbital in the same way would contain a minor p_z component. However the $d_{x^2-y^2} \leftarrow p_z$ transition is $\delta \leftarrow \sigma$ and is forbidden. The p_z orbital would provide intensity to the extent that the a_1 orbital mixed in the d_{z^2}. If the term in eq 5 is the principal origin of this intensity for the *x*-polarized band, the mixing coefficient C_x must be quite small to account for the modest intensity observed since the transition moment integral in eq 5 corresponds to a strongly dipole-allowed transition.

The band in *c-x* polarization was clearly not symmetric, especially at room temperature. A component was resolved with a maximum at 32,100 cm^{-1} with roughly 60% of the intensity of the stronger component. In contrast, its intensity dropped at lower temperatures indicating largely a vibronic excitation. This transition is logcially assigned as $^1A_2 \leftarrow {}^1A_1$ ($\sigma^* \leftarrow d_{xz}$). From the possible polarizations indicated in Table I it is seen that this transition has a zero ligand field transition moment but can be excited vibronically with both *x* and *z* polarization. Note that the transition $^1B_1 \leftarrow {}^1A_1$, seen in *a-z* polarization, is completely forbidden in *x* polarization. This $^1B_1$ state and the $^1A_2$ state are derived from the degenerate ^1E_g pair in D_{4h} symmetry. The expression for the temperature dependence of a transition[15] excited vibronically by a vibration of frequency ν_i is

$$f(T)/f(0) = \coth(h\nu_i/2kT) \quad (6)$$

The ratio of intensities indicates a $\bar{\nu}_i$ of 215 cm^{-1}. A vibration with the required B_2 symmetry and $\bar{\nu}$ 230 cm^{-1} has been reported.[16,17] It is apparent that the $^1A_2$ and $^1B_1$ states are not greatly split by the C_{2v} symmetry, and our program was not able to resolve two components for the band in *a-z* polarization.

The low absorption in the region of 20,000-26,000 cm^{-1} is due to excitation of the "spin-forbidden," primarily triplet states. Its temperature dependence indicate that these bands are due mostly to vibronic excitation. Selection rules governing the intensity of a singlet state do not carry over to the corresponding triplet states. Also, there are 9 states in this region where only one or two poorly resolved bands can be discerned for each polarization: any attempt for a more detailed assignment in the spin-forbidden would scarcely be meaningful.

Characterization of the Red Form of $KPt(NH_3)Cl_3 \cdot H_2O$. Upon prolonged crystallization of $KPt(NH_3)Cl_3 \cdot H_2O$, there are formed crystals with the red sections noted by Jorgensen.[6] The crystals frequently formed flat rectangular plates with large 010 faces, extended in the *a* direction which is the stacking axis for the anions. The red sections were frequently a pair of isosceles triangles based on the short edge of each crystal. When the crystals are observed under light with *a* polarization, the triangular sections are bright red and the remainder of the crystal is a bright yellow. When the polarization is rotated to the *c* direction, the color is a uniform orange and not the slightest inhomogeneity can be discerned by the eye. In this polarization the absorption in the visible region must be essentially the *c-x* spectrum shown in Figure 4 for a yellow crystal. In other instances with *a* polarization, streaks of red can be seen running through yellow sections. Red sections of the crystals were investigated. In several instances small red sections were broken out and subjected to a thermogravimetric analysis. These analyses agreed with the analysis of $KPt(NH_3)Cl_3 \cdot H_2O$ to within the experimental error. Weissenberg X-ray diffraction photographs revealed the superlattice lines mentioned earlier. Finally, small red sections were dissolved in aqueous KCl for determination of the ultraviolet spectra. Here, differences between the red sections and the yellow were clearly evident. The absorption intensity at lower wave lengths was much higher than for the "pure" yellow compound whose spectrum appears in Figure 1. For the very red crystals

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(15) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 187.

(16) J. Hiraishi, I. Nakagawa, and S. Takehiko, *Spectrochim. Acta, Part A*, 24, 819 (1968).

(17) R. G. Denning and M. J. Ware, *Spectrochim. Acta, Part A*, 24, 1785 (1968).

Table IV. Resolution and Assignments of the Absorption Bands in the Aqueous Spectra of $Pt(NH_3)Cl_5^-$ and $PtCl_6^{2-}$

$PtCl_6^{2-}$ (O_h)[a]				$Pt(NH_3)Cl_6^-$ (D_{4v})			
Energy, $\bar{\nu}$, cm^{-1}	Molar absorp, ϵ, cm^{-1} M^{-1}	Oscillator strength, 10^4f	Assignment, ground state $^1A_{1g}$	Energy, $\bar{\nu}$, cm^{-1}	Molar absorp, ϵ, cm^{-1} M^{-1}	Oscillator strength, 10^4f	Assignment, ground state $^1A_1$
22,100	50	9	$^3T_{1g}$ $(\sigma^* \leftarrow d)$	21,600	35	3	$^3A_2$ $(d_{x^2-z^2} \leftarrow d_{xz})$ ^3E $(d_{x^2-z^2} \leftarrow d_{xy,yz})$
28,000	490	70	$^1T_{1g}$ $(\sigma^* \leftarrow d)$	29,100	540	150	$^1A_2$ $(d_{x^2-z^2} \leftarrow d_{xz})$ ^1E $(d_{x^2-z^2} \leftarrow d_{xy,yz})$
38,200	24,500	5700	$^1T_{1u}$ $(\sigma^* \leftarrow t_{1u}, t_{2u}, \text{Cl } \pi)$	36,100	4,300	1200	$^1A_2$ $(d_{x^2-z^2} \leftarrow b_2, \text{Cl } \pi)$
				41,000	9,200	1900	^1E $(d_{x^2-z^2} \leftarrow e_u, \text{Cl } \pi)$
				47,000	20,000	5600	$^1A_2$, ^1E $(d_{y^2} \leftarrow \text{Cl } \pi)$

[a] Reference 21.

the band at 33,400 cm^{-1} had disappeared as an intense charge-transfer band obscured it. It was concluded that the solution contained some platinum(IV) complex in addition to $Pt(NH_3)Cl_3^-$. Other observations seemed relevant. When solutions of $KPt(NH_3)Cl_3$ stood in air, a yellow powder slowly precipitated which was analyzed to give the formula $KPt(NH_3)Cl_5 \cdot H_2O$. When HCl was added to the solutions, usually the platinum(IV) complex was formed in a few days. Presumably an air oxidation occurs according to the reaction

$$2Pt(NH_3)Cl_3^- + 4H^+ + 4Cl^- + O_2 \rightarrow 2Pt(NH_3)Cl_5^- + 2H_2O \tag{7}$$

The aqueous ultraviolet spectrum of $Pt(NH_3)Cl_5^-$ is given in Figure 1. The compositions of red sections as mixtures of $KPt(NH_3)Cl_3 \cdot H_2O$ and $KPt(NH_3)Cl_5 \cdot H_2O$ were obtained from the molar absorptivity of the solutions at 29,000, 33,000, and 36,000 cm^{-1}. Different samples possessed different analyses which ranged from <0.5 up to 7% for a very dark red fragment. Agreement of compositions calculated from the measurements at the three wave lengths was generally to within 5%.

When the platinum(II) and platinum(IV) compounds were dissolved in nearly equal amounts, crystals with a copper-like luster were formed as the solution evaporated. Analysis by the thermogravimetric analysis corresponded fairly closely to a formula $KPt(NH_3)Cl_4 \cdot H_2O$. Under a polarizing microscope the crystals exhibited in one polarization an orange color resembling the *c* polarization of $KPt(NH_3)Cl_3$. With the polarizer rotated 90° even the thinnest sections obtainable were opaque black. These optical properties resemble somewhat those of the green crystals of $Pt(en)Br_3$ where it has been shown[18] that octahedral platinum(IV) complexes stack alternately with planar platinum(II) molecules and Pt–Pt separations of 5.60 Å. A crystal structure determination is under way and at present indicates an alternate stacking of ions with a Pt–Pt distance of 5.22 Å. These crystals are apparently exhibiting the mixed-valence type spectra which Robin and Day[19] have characterized as class II and which involve an electron transfer from Pt^{II} to Pt^{IV}. It has been concluded from this evidence that the red crystals are a solid-state solution with the octahedral $Pt(NH_3)Cl_5^-$ ion randomly displacing planar $Pt(NH_3)Cl_3^-$ ions in the structure.

Werner[20] described the transient appearance of unusual crystallites during the cooling of solutions of $KPt(NH_3)Cl_3$ to which a lesser quantity of $KPt(NH_3)Cl_5$ had been added. From these observations he concluded that the two compounds formed an "addition" compound. However, he was unable to collect any crystals of this "addition" compound for analysis or other characterization.

Spectrum of Aqueous $Pt(NH_3)Cl_5^-$. Since the red crystals are believed to contain $Pt(NH_3)Cl_5^-$, the spectral assignments of this free ion need consideration. A comparison of the bands resolved from the spectrum in Figure 1 and the transition assignments with those of $PtCl_6^{2-}$, reported by Jorgensen,[21] are presented in Table IV. With the substitution of one Cl^- ligand by NH_3, the local symmetry of the platinum is reduced from O_h to D_{4v}. The degeneracy of the lowest unfilled antibonding orbitals, e_g under O_h, is broken to give a_1 and b_1 orbitals. For convenience in comparison with the planar $Pt(NH_3)Cl_3^-$ case, the *y* axis will be placed unconventionally along the symmetry axis so the a_1 orbital will involve a d_{y^2} and the b_1 orbital will involve the $d_{x^2-z^2}$. The effect of the NH_3 group which is higher in the spectrochemical series is to raise the energy of the a_1 orbital a considerable amount, as is shown in Figure 2, and not to change greatly the relative energy of the other d orbitals or the Cl π orbitals. The pair of e orbitals, based on $d_{xy,yz}$, are placed slightly below the b_2 orbital of the t_{2g} set in O_h because they will presumably have lost some π-antibonding character with the replacement of a Cl^- by an NH_3. As a consequence, there has been very little energy shift in the bands which have been assigned as the spin-forbidden and the spin-allowed $d_{x^2-z^2} \leftarrow d$ transitions. There has been a loss of inversion symmetry which should increase the intensity for this type of transition. However, some intensity is lost since transitions to the d_{y^2} orbital are now at much higher energies and are obscured under stronger bands. In place of the single charge-transfer band observed at 38,200 cm^{-1} with $PtCl_6^{2-}$, there is a weaker absorption which was resolved into two components for $Pt(NH_3)Cl_5^-$ whose transition energies bracket that for the $PtCl_6^{2-}$ band. The $PtCl_6^{2-}$ band is considered to arise from transitions of electrons from t_{1u} and t_{2u} linear combinations of Cl π-orbitals to the $e_g\sigma$-antibonding orbitals. It is proposed that the weaker band at 36,100 cm is $^1A_2 \leftarrow {}^1A_1$ $(b_1^* \leftarrow b_2$, Cl $\pi)$. The b_2 orbital derives from t_{2u}, and this is the only transition to $d_{z^2-x^2}$ with *y* polarization. The stronger band at 41,000 cm^{-1} then probably corresponds to transitions $^1E \leftarrow {}^1A_1$ $(b_1^* \leftarrow e$, Cl $\pi)$. The e orbitals arise from both the t_{1u} and the t_{2u} orbitals. The intense band at 47,000 cm^{-1} where $PtCl_6^{2-}$ has a low absorption then can be attributed to the charge-transfer transition $a_1^* \leftarrow$ Cl π, where a_1^* is the antibonding orbital which includes the nitrogen σ orbital.

Polarized Spectrum for a Red Crystal. Figure 6 provides the polarized spectra of a red crystal at both 15 and 300°K.

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(18) T. D. Ryan and R. E. Rundle, *J. Amer. Chem. Soc.*, **83**, 2814 (1961).

(19) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, 10, 248 (1967).

(20) A. Werner, *Z. Anorg. Chem.*, **12**, 48 (1896).

(21) C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

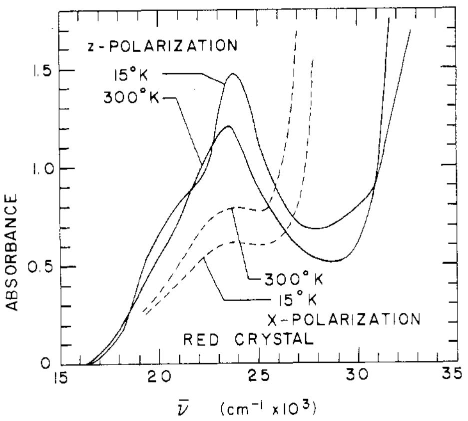

Figure 6. Polarized crystal spectra for a red crystal, $K[Pt(NH_3)Cl_3]_{1-x}[Pt(NH_3)Cl_5]_x \cdot H_2O$.

The crystal was too thick to obtain the band maximum in *c-x* polarization. It is noted that the absorption for the *c-x* polarization decreases at lower temperatures. Since no visual difference is apparent for the *c* polarization of the red and yellow sections, the thickness of the crystal was calculated to be 17.2 μ from the *c* absorbance at 23,500 cm^{-1} and the molar absorptivity from Figure 4. The red color is seen to be the result of a band in the *a-z* polarization with a maximum at 23,500 cm^{-1}. At lower temperatures this band was a higher peak which has been shifted to 23,800 cm^{-1}. Therefore, the major component of this band appears to be dipole allowed. There is a shoulder appearing at about 20,000 cm^{-1} at low temperature, and the valley at 30,000 cm^{-1} was not so well defined at lower temperatures. However, additional crystal spectra will be required before such minor features can be accepted as real. If this absorption is due to an impurity in $KPt(NH_3)Cl_3 \cdot H_2O$ of about 1%, the absorption corresponds to a molar absorptivity of approximately 6000 cm^{-1} (mol of impurity/l.)$^{-1}$; *i.e.*, it is a strongly allowed transition. This absorption is therefore much greater than that of a free $Pt(NH_3)Cl_5^-$ ion at this wave length. The spectra for a red crystal are especially valuable because they provide the mixed-valence band in a system where the Pt^{IV} complex is present in a dilute solution, but for which the Pt^{IV} ion has the same orientation as in the crystal with $Pt^{IV}:Pt^{II} = 1:1$. Otherwise, an impossibly thin crystal would be required to obtain the mixed-valence band.

The short distance of 5.22 Å between the Pt^{II} and Pt^{IV} atoms where the Pt^{IV}-Cl is probably *ca.* 2.32-2.35 Å indicates a distance of *ca.* 2.9 Å between the Pt^{II} and Cl. This distance is short enough to imply some bonding between the complexes. The chloride ligands along the *z* axis would serve as bridging ligands. In forming the bond, the pair of electrons in the nonbonded σ orbital of the chloride would be donated to the bond which would involve the lowest empty σ orbital of the Pt^{II} which is the p_z. It is expected that as in the case of $Pt(en)Br_2 \cdot Pt(en)Br_4$, the bridge would not be symmetric,[18] and the two complexes would retain their identity in the solid state.[22]

The polarization of the mixed-valence band in the *z* direction implies a transition corresponding to $\sigma(Pt^{IV}) \leftarrow \sigma(Pt^{II})$. The highest filled orbital with σ symmetry along the *z* axis for the Pt^{II} complex is the d_{z^2} and the lowest unfilled orbital for the Pt^{IV} complex is the σ-antibonding orbital based on $d_{x^2-z^2}$. Since the transition is so intense and there must be negligible overlap between the platinum orbitals separated by >5 Å, the transition must involve the σ orbitals 3s and $3p_z$ of the bridging chloride as well. For the $Pt(NH_3)Cl_3^-$ complex the d_{z^2} orbital, as shown in Figure 2, is believed to be lowest d orbital. Now there is a filled set of $d_{xz}d_{yz}$ orbitals, which have π symmetry with respect to the *z* axis. If an electron is excited from the d_{z^2} orbital into an unfilled σ orbital, there should be $\sigma \leftarrow \pi$ transitions involving the $d_{xz}d_{yz}$ electrons which are of the same order of intensity in *x* and *y* polarizations. The fact that there is no evidence for such a transition below 30,000 cm^{-1} implies that there has been a destabilization of the highest filled σ orbital with respect to the other orbitals which are primarily d orbitals. That such a relative destabilization occurs appears reasonable when it is noted that in the case of a symmetric bridge, between two equivalent Pt^{III} complexes, the two σ orbitals on the different complexes become degenerate. Thus, although there may be intercomplex electron transfers which are polarized normal to the stacking direction, they are masked by the other intense transitions in the complexes. The luster of the 1:1 mixed-valence complexes may well be only a consequence of the high reflectance associated with an intense absorption in the visible region rather than true metallic luster. The Pt^{IV} content is so low in the red crystals that the absorption normal to the chains is not altered sufficiently to give a discernible change in the color of crystals when viewed with *c*-polarized light.

In a comparison of the polarized spectra of the Cossa's salts with those of K_2PtCl_4, it should be indicated that the absorption is much higher with the $Pt(NH_3)Cl_3^-$ ions so that much thinner crystals have been required. There was good evidence from the temperature dependence of intensities for Cossa's salt that in one band the ligand field excitation was as effective as the vibronic mechanism. The rigor of the ligand field and vibronic selection rules which apply to the transition at 28,800 cm^{-1} in the yellow salt is impressive. The applicability of the selection rules for the present case provides justification for the assignment of the intermolecular electron-transfer transitions in $Pt(en)Cl_2$ which were based on the molecular selection rules and the temperature dependence of the bands.[3]

For $KPt(NH_3)Cl_3 \cdot H_2O$ there was no evidence of vibrational structure in any band such as occurs for some bands of K_2PtCl_4. However, such vibrational structure corresponds to the Franck-Condon effect on the totally symmetric vibration modes. Whereas $PtCl_4^{2-}$ has only one totally symmetric mode, the $PtNCl_3$ framework has four. Therefore, in part, such vibrational structure may be lost from the number of A_1 vibrational progressions. The identification of an anion chain with the cations packed around it is somewhat analogous to Wolffram's red salt, $[Pt(C_2H_5NH_2)_4Cl_2][Pt(C_2H_5NH_2)_4]Cl_4 \cdot 4H_2O$, in which there is a cation chain of alternating valence complexes.[19] In addition, an unstable green compound, Cs_2PtCl_5, was reported by Wohler and Martin[23] but it has not been further characterized.

Registry No. $KPt(NH_3)Cl_3 \cdot H_2O$ ("yellow Cossa's salt"), 20574-25-8; $KPt(NH_3)Cl_5 \cdot H_2O$, 36223-08-2; $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5] \cdot 2H_2O$, 36223-09-3.

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