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Notes

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Electronic Structure of the Tetracyanoplatinate(II) Anion

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The electronic absorption bands of compounds containing the square-planar $Pt(CN)_4{}^{2-}$ ion have received considerable experimental and theoretical study, since the anion is a model for planar complexes with strong-field ligands.[1-11] Of special interest has been the observation of spectral shifts in the ultraviolet electronic absorption spectra for various alkali and alkaline earth salts arising from an axial interaction between stacked complex ions in the solid state.[6,12]

Recent work on the metallic one-dimensional platinum compounds, $K_2Pt(CN)_4X_{0.3}{\cdot}3H_2O$ (X = Cl, Br), in which planar tetracyanoplatinate units form linear chains of platinum atoms in one dimension,[13,14] has provided further impetus to determine the electronic structure of this ion.[11] The suggestions of a low-temperature transition to a Peierls insulator together with evidence for one-dimensional metallic properties at room temperature[14] has made the tetracyanoplatinates the subject of intense study recently.

Two theoretical MO calculations for $Pt(CN)_4{}^{2-}$ which included spin–orbit coupling implicitly[8,10] suggest a number of states for which spectroscopic transitions have not been observed. Self-consistent field, Xα scattered-wave calculations also predict unobserved spectroscopic states.[11]

These results have prompted us to reinvestigate the ultraviolet electronic absorption spectrum of the $Pt(CN)_4{}^{2-}$ ion in aqueous and nonaqueous media using an interacting computer curve resolving program.

Experimental Section

Tetrabutylammonium tetracyanoplatinate(II), **1**, was prepared from commercially available $K_2Pt(CN)_4{\cdot}3H_2O$, **2**, by a literature method.[5] Compounds **1** and **2** were purified prior to use by multiple recrystallizations.

Ultraviolet absorption spectra at 77 K were obtained on a Cary 15 recording spectrophotometer using a specially constructed low-temperature cell holder with a massive copper heat sink in contact with a liquid nitrogen reservoir. In this apparatus, 1-mm path length quartz absorption cells were filled with solutions in 9:1 (volume) methanol–water (a low-temperature glass) and cooled until the solutions solidified; the entire apparatus was evacuated to maintain constant temperature. Room-temperature absorption spectra were obtained in the usual manner.

Spectrophotometric data are presented via mechanical encoding to the analog inputs of a spectrophotometer interface (Data Graphics 9158) which provides analog to digital converted data at the output as parallel BCD (binary coded decimal) for further processing, serialization, and decoding by a programmable interface (Data Graphics 305). The programmable interface outputs the data in USASCII coding suitable for an automatic send–receive terminal (Texas Instruments ASR 733). This ASR terminal receives USASCII coded data for off-line storage on magnetic tape cassettes and transmits data to a Sigma 9 computer for processing and plotting.

An interactive Gaussian curve resolving program was used to deconvolute the observed spectral envelopes into a minimum number of Gaussian bands, which represent the various electronic absorption transitions for $Pt(CN)_4{}^{2-}$. This program performs successive interactions to obtain the best possible fit between the observed spectrum and the predicted spectrum, which is the sum of all Gaussian components. A standard deviation for the fits was generally $\sigma \approx 0.001$.

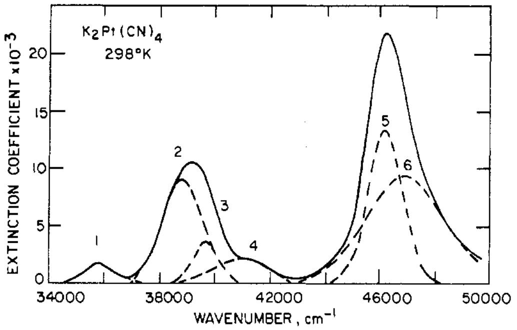

Figure 1. Deconvoluted electronic spectra for a 3.7×10^{-4} M solution of $K_2Pt(CN)_4$ in aqueous solution at room temperature.

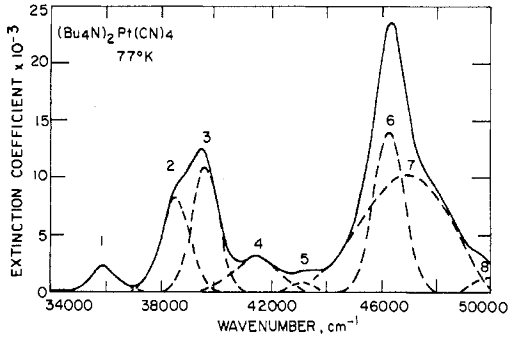

Figure 2. Deconvoluted electronic spectra for a 0.98×10^{-4} M solution of $[(n\text{-}C_4H_9)_4N]_2Pt(CN)_4$ in 9:1 CH_3OH–H_2O at 77 K.

Results and Discussion

The solution electronic absorption spectra for $K_2Pt(CN)_4$ and $(Bu_4N)_2Pt(CN)_4$ are presented in Figures 1 and 2 and in Table I. The solid curve in Figure 1 represents the absorption envelope for a 3.7×10^{-4} M solution of $K_2Pt(CN)_4$ in water at 298 K. The spectrum is plotted as extinction coefficient (M^{-1} cm^{-1}) against energy (wavenumber). The dashed curves represent the Gaussian components from the curve fitting analyses. These may be correlated with individual electronic transitions between energy levels in $K_2Pt(CN)_4$.

The assumption that electronic transitions may be represented by Gaussian curves has been discussed by Siano and Metzler[15] and Siano.[16] This approximation is reasonable for bands which show no skewness. For skewed bands a log-normal approximation is preferred. The use of different functions does not alter the number of bands but may change relative positions slightly. From Figure 1 the absorption region between 37000 and 41000 cm^{-1} contains a band that clearly shows asymmetry. This has been resolved into two components identified as bands 2 and 3. Similarly, for the energy region between 44000 and 50000 cm^{-1} the asymmetric band has been

Table I. Electronic Absorption Energy Maxima, Extinction Coefficients, and Oscillator Strengths for $K_2Pt(CN)_4$ and $(Bu_4N)_2Pt(CN)_4$[a]

Band	$K_2Pt(CN)_4$ (H_2O, 298 K)			$(Bu_4N)_2Pt(CN)_4$ (H_2O, 298 K)			$(Bu_4N)_2Pt(CN)_4$ (MeOH–H_2O, 77 K)			$(Bu_4N)_2$-$Pt(CN)_4$[b]
	ν_{max}	ϵ	f	ν_{max}	ϵ	f	ν_{max}	ϵ	f	ν_{max}
1	35 805	1 550	0.008	35 785	1 525	0.007	35 925	1 975	0.008	35 835
2	38 835	9 175	0.062	38 740	10 915	0.070	38 560	8 355	0.040	38 435
3	39 655	3 495	0.014	39 595	4 940	0.021	39 620	10 975	0.048	39 555
4	40 940	2 040	0.019	40 965	2 320	0.021	41 435	3 065	0.023	41 440
5				43 500			43 215	715	0.023	45 450
6	46 175	13 600	0.078	46 128	17 570	0.100	46 285	13 870	0.064	46 275
7	46 875	9 440	0.123	46 760	10 725	0.152	46 920	10 585	0.152	46 945
8				(50 400)[c]			(50 000)[c]			

[a] Energy maxima given in wavenumbers; extinction coefficient in M^{-1} cm^{-1}. Energy maxima accurate to ±10 cm^{-1}; ϵ and f accurate to ±10%. Low-temperature ϵ and f values corrected for solvent contraction at 77 K. Oscillator strengths calculated by $f = 4.3 \times 10^{-9} F \int \epsilon \, d\nu$ where $F = 9n/(n^2 + 2)^2 = 0.843$: A. Rubinowicz, *Rep. Prog. Phys.*, **12**, 233 (1948–1949). [b] Thin crystalline film (77 and 298 K). [c] Parentheses denote less certain values.

Table II. Energy Levels, Metal-to-Ligand Charge-Transfer Transition Assignments, and Symmetry labels for the $Pt(CN)_4^{2-}$ Anion[a]

		Assignments and symmetry labels				
Band	Transition energy[b] (this paper)	Isci and Mason[8]	Interrante and Messmer[11]	Piepho et al.[10]	Mason and Gray[5]	Moncuit[4]
1	35 785	(E_u')	$2b_{2g} \to 3a_{2u}$ (E_u')	$a_{1g} \to a_{2u}$ (E_u')	$b_{2g} \to a_{2u}$ (E_u') $(^1B_{1u})$*	$a_{1g} \to a_{2u}$ (E_u') $(^1A_{2u})$*
2	38 740	(A_{2u}', E_u')	$2e_{2g} \to 3a_{2u}$ (E_u) (E_u', A_{2u}')	$e_g \to a_{2u}$ (E_u', A_{2u}')	$e_g \to a_{2u}$ (E_u)	$e_g \to a_{2u}$ (E_u)
3	39 595	(B_{1u}')	$2b_{2g} \to 3a_{2u}$ (B_{1u})			
4	40 965		$1a_{2g} \to 3a_{2u}$ (A_{2u}', E_u')		$a_{1g} \to a_{2u}$ (A_{2u})	$a_{1g} \to e_u$ (E_u)
5	43 500		$1a_{2g} \to 3a_{2u}$ (A_{1u})	(E_u)		
6	46 128	(A_{2u}, E_u)	Three singlet Six triplet	$e_g \to a_{2u}$ (E_u') $a_{1g} \to a_{2u}$ (A_{2u})	$b_{2g} \to e_u$ (E_u)	$b_{2g} \to e_u$ (E_u)
7	46 760	(B_{1u})		$b_{2g} \to a_{2u}$ (B_{1u})		
8	50 400		$5a_{1g} \to 3a_{2u}$ (A_{2u})			

[a] Primes on symmetry labels indicate spin–orbit coupling has been considered; all symmetry labels employ double rotational group notation, except asterisks which denote single rotational group rotation. [b] Energies in cm^{-1}, at 298 K.

resolved into bands 5 and 6. Mason and Gray[5] have previously suggested the presence of bands 2 and 3, from low-temperature absorption spectral results. Isci and Mason[8] reported a shoulder near 47000 cm^{-1} for **1** in acetonitrile at room temperature. Our curve fitting results agree that for $K_2Pt(CN)_4$ in aqueous solution at room temperature there are at least six absorption bands.

The results for a low-temperature absorption spectrum of $(Bu_4N)_2Pt(CN)_4$ in a 9:1 mixture of methanol and water at 77 K are shown in Figure 2. This spectrum shows quite clearly the asymmetry in the 37000–41000- and 44000–50000-cm^{-1} absorption regions previously discussed. Bands 5 and 8 (Figure 2) have not been reported previously. The spectra obtained for **1** at room temperature and at 77 K in EPA (a low-temperature glass solvent), in water, cast as a film on quartz plates are nearly identical. This suggests that hydrolysis and ion pairing play an insignificant role in the solution behavior of the $Pt(CN)_4^{2-}$ ion.

In Table I are presented the maxima of the absorption bands, molar extinction coefficients, ϵ, and oscillator strengths, f, for **1** and **2** in solutions at room temperature and low temperature and for **1** as a thin film. In Table II are presented the assignments of the transitions between the energy levels for the $Pt(CN)_4^{2-}$ anion, as suggested by various authors. Symmetry labels are derived from double rotational group notation; primes on symmetry labels denote a double-group state derived from spin–orbit splitting of appropriate triplet states.

In spite of the fact that the $Pt(CN)_4^{2-}$ anion has been the subject of considerable study over the past decade, there is still no general agreement regarding the nature of the electronic transitions nor the excited electronic energy levels and their orderings. Early measurements made by Jorgensen,[1] Ryskin et al.,[3] Moncuit,[4] and Mason and Gray[5] all agree on the existence of five rather intense bands in the region of 34000–50000 cm^{-1}. The high intensity of these bands led the authors to identify them with metal to ligand charge-transfer bands. Charge-transfer transitions from ligand to metal have been rejected, since their energies are known to be much higher in the case of the isoelectronic $Au(CN)_4^-$.[17] The ordering of the metal MO's varies; Mason and Gray[5] have proposed a level ordering of $b_{1g}(d_{x^2-y^2}) >> b_{2g}(d_{xy}) > e_g(d_{xz},d_{yz}) > a_{1g}(d_{z^2})$, which is in agreement with the ordering suggested by Interrante and Messmer[11] based upon Xα scattered-wave calculations. Piepho et al.[10] and Isci and Mason[8] preferred an ordering in which the $a_{1g}(d_{z^2})$ lies above the e_g and b_{2g} levels. The calculation of Interrante and Messmer[11] is an ab initio self-consistent field (SCF) treatment based on a statistical approximation for exchange correlation (the Xα potential) together with a multiple scattered-wave procedure for wave function matching, applied to yield molecular spin orbitals and energies as solutions of the Schrödinger equation. These calculations do not implicitly include spin–orbit coupling. Piepho et al.[10] and Isci and Mason,[8] on the other hand, implicitly included spin–orbit coupling in their molecular orbital calculations in which they employ estimated energies for several unperturbed states and values for spin–orbit parameters, to provide a best fit to the unobserved bands.

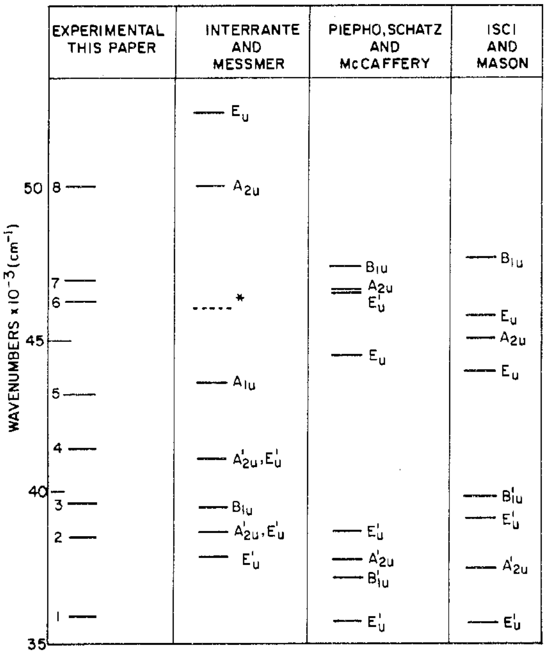

Figure 3. Correlation of the observed electronic transitions with the calculation of Interrante and Messmer,[11] Piepho, Schatz, and McCaffery,[10] and Isci and Mason.[8] Asterisk signifies three singlet and six triplet energy levels in this region.

The assignment for the long-wavelength transition near 35800 cm^{-1} is still in question because of the uncertainty in the ordering of the d levels. It is agreed[8,10,11] that the transition terminates on an a_{2u} π^* ligand level. The extinction coefficient and oscillator strength for this transition are small (Table I), and this is in qualitative agreement with the assignment as a singlet–triplet transition. Piepho et al.,[10] Isci and Mason,[8] and Interrante and Messmer[11] assigned the transitions for bands 2 and 3 as $e_g \rightarrow a_{2u}$, giving rise to E_u' and A_{2u}' states. Interrante and Messmer assigned both singlet and triplet transitions to the 38835-cm^{-1} band. The shoulder near 41000 cm^{-1} had not been assigned with certainty. The calculations of Piepho et al.[10] do not account for this transition, although they speculated on possible transitions. Isci and Mason[8] and Interrante and Messmer[11] on the other hand have calculated energy levels that agree fairly well with this shoulder and Interrante and Messmer[11] assigned the transition as $a_{2g} \rightarrow a_{2u}$ with symmetry labels (A_{2u}', E_u'). The less intense band near 43500 cm^{-1} previously unreported in the literature can be accounted for by Piepho et al.[10] and Isci and Mason[8] who assigned a symmetry label of E_u' whereas Interrante and Messmer[11] have assigned the transition in this region as $a_{2g} \rightarrow a_{2u}$ with symmetry label A_{1u}.

The assignments of the experimentally observed transitions in the region 44000–50000 cm^{-1} are less clear. Interrante and Messmer[11] have calculated three singlet and six triplet energy levels to lie in that region but did not assign transitions for them. Isci and Mason[8] have calculated states near 45000 (A_{2u}), 45700 (E_u'), and 47600 cm^{-1} (B_{1u}), although they did not report the assignment of transitions at energies greater than these three.

The additional transition present at an energy greater than 50000 cm^{-1}, band 8, is in closer agreement with the calculations of Interrante and Messmer.[11] They have calculated energy states at 50800 and 52400 cm^{-1}. The transition at 50800 cm^{-1} has been assigned as $a_{1g} \rightarrow a_{2u}$ (A_{2u}).[11]

Figure 3 shows the energy levels for states in $Pt(CN)_4{}^{2-}$ obtained by curve fitting experimental data. Shown also are the energy states calculated by Piepho et al.,[10] by Isci and Mason,[8] and by Interrante and Messmer.[11] This figure shows the agreement between theory and experiment for the two very different approaches used by these authors. The calculations of Piepho et al.[10] and Isci and Mason[8] agree with the experimental results at low energies better than at higher energies, whereas calculations based on the Xα scattered-wave approach agree better at the higher energies. The latter calculations did not implicitly include spin–orbit coupling, which may have improved the agreement with the experimental data.

The assignments of the metal to ligand charge-transfer electronic absorption transitions for the $Pt(CN)_4{}^{2-}$ anion are still subject to question. It is hoped that this additional experimental evidence may stimulate further theoretical calculations on the interesting tetracyanoplatinate anion.

Registry No. $K_2Pt(CN)_4$, 562-76-5; $(Bu_4N)_2Pt(CN)_4$, 21518-40-1.

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Extraction of Molybdenum(VI) from Hydrochloric Acid Solutions by Triisooctylamine in Organic Diluents

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There exist only a few detailed investigations of the extraction of molybdenum(VI) by long-chain alkylammonium salts, and these deal mainly with the influence of acidity and diluents on the extraction.[1-7] For example, the equilibria involved in extracting Mo(VI) from aqueous nitric acid solutions were found to depend upon the diluent.[1,8]

In nonpolar diluents, third-phase formation was observed when the aqueous molybdenum(VI) concentration was increased. No definite formula could be given to the organic compound as was found from molecular weight determinations. In 1,2-dichloroethane and 1,2-dichlorobenzene, no third-phase formation occurred nor did extraction lead to aggregation.

In hydrochloric acid medium, the formation of a third phase has been reported in the extraction of Mo(VI) by hydrochloride salt solutions of triisooctylamine in benzene and xylene.[9] This, however does not occur when extractions are performed with those diluents at a high acidity (from 1 to 6 M HCl) or at relatively low acidity (0.01 M HCl) when the ammonium salt is dissolved in moderately polar diluents.[10]