(3) R. H. Magnuson and H. Taube, *J. Am. Chem. Soc.*, **94**, 7213 (1972).
(4) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967); *Electrochim. Acta*, **13**, 1005 (1968).
(5) N. S. Hush and G. C. Allen, *Prog. Inorg. Chem.*, **8**, 357 (1967).
(6) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).
(7) R. W. Callahan, Ph.D. Thesis, The University of North Carolina, Chapel Hill, N.C., 1975; R. W. Callahan, R. Keene, and T. J. Meyer, submitted for publication.
(8) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
(9) R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 7829 (1974); R. W. Callahan, G. M. Brown, and T. J. Meyer, *Inorg. Chem.*, **14**, 1443 (1975).
(10) The assumption that $T\Delta S^{\circ\prime} \approx 0$ is probably resonable. The standard entropy differences between 2+ and 3+ ions in water for the couples $Ru(bpy)_3^{3+}$–$Ru(bpy)_3^{2+}$ and $Ru(NH_3)_6^{3+}$–$Ru(NH_3)_6^{2+}$ are +0.4 ± 2.0 and +4.1 ± 1.9 eu, respectively.[11]
(11) D. K. Lavallee, C. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **12**, 570 (1973).
(12) The IT and $\Delta G^{\circ\prime}$ data are in different media, but E_{op} is apparently relatively insensitive to medium effects. E_{op} is the same within experimental error in 0.1 M $(n\text{-Bu})_4NPF_6$–CH_3CN and in pure acetonitrile.
(13) $E_{1/2}(1)$ for the symmetrical dimer, $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+/2+}$ (Table I), is disfavored by a statistical factor of 2, since there are two equivalent sites for redox. Thus $\mathcal{E}_2^{\circ\prime} = E_{1/2}(1)_{sym} + 0.059 \log 2 \simeq E_{1/2}(1)_{sym} + 0.02$ V.

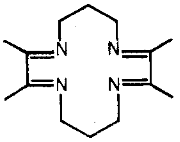
Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Catalysis of "Franck–Condon Forbidden" Electron-Transfer Reactions by Macrocyclic Cobalt(II) Complexes[1]

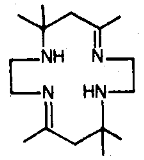
D. Paul Rillema and John F. Endicott*

Received November 6, 1975 AIC50805+

In an earlier study[2] we observed that the Cr^{2+} reduction of $Co([14]tetraeneN_4)(NH_3)_2^{3+}$ [3] was autocatalytic. We were able to demonstrate in this system that the significance of the catalytic pathway increased with $[Co([14]tetraeneN_4)(OH_2)_2^{2+}]$ and we suspected the reactive intermediate to be a cobalt(I) complex. The small rates for outer-sphere Cr^{2+} reductions of cobalt(III) complexes may be attributed to relatively large inner-sphere reorganizational barriers.[2] The observation of a catalytic pathway suggests the existence of a reaction channel in which the apparent Franck–Condon constraints may be somewhat relaxed. This possibility and the novel possibility of finding a convenient means for generating and studying reactive cobalt(I) species in aqueous solution have led us to investigate these effects further. For these investigations we have selected the $Co([14]tetraeneN_4)(OH_2)_2^{2+}$-catalyzed Cr^{2+} reduction of $Co([14]dieneN_4)(NH_3)_2^{3+}$ because (1) the net reaction is not autocatalytic and thus relatively convenient to investigate quantitatively and (2) the Cr^{2+}–$Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}$ reaction has a larger apparent reorganizational barrier[2] than the one we originally discovered, so it could be more susceptible to catalytic effects. This report of our studies has been prompted by the recent elucidation of the chemistry of $Co^I([14]tetraeneN_4)$ and $Co^I([14]dieneN_4)$ using pulse radiolytic techniques.[4]



$[14]tetraeneN_4$



$[14]dieneN_4$

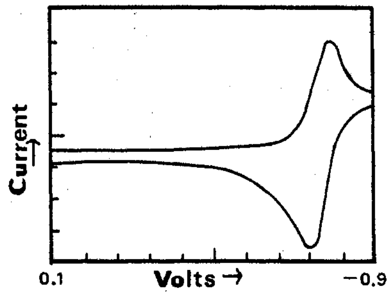


Figure 1. Cyclic voltammogram for the $([14]tetraeneN_4)Co^{II}$–$([14]tetraeneN_4)Co^I$ couple in water; sweep time 1 division/s; 1 μA/division; voltage range +0.1 to −0.9 V vs. SCE.

Experimental Section

The complexes $[Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2](ClO_4)_3\cdot 2H_2O$[2] and $[Co([14]tetraeneN_4)(ClO_4)_2]\cdot 2H_2O$[5] were prepared as described elsewhere.

Preparation of Cr^{2+} solutions, sample-handling techniques, most kinetic procedures, and electrochemical techniques were similar to those described previously.[2,5–7] $Cd(NO_3)_2$ was used to calibrate the potential output of the Chemtrix SSP-2; for the present study we equipped the instrument with an external voltmeter to improve the precision of voltage measurements.

Solutions of Cr^{2+}, $Co^{II}([14]tetraeneN_4)$, and Cr^{3+} were mixed in a 1-cm cell prior to the addition of a solution of $Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}$. The ionic strength was 0.82 M in $HClO_4$ and $NaClO_4$. The reaction was followed at the 330 nm (ϵ 2.4 × 10^3) charge-transfer absorption maximum[6a,7] of the $Co^{II}([14]\text{-}4,11\text{-}dieneN_4)$ product.

Similar procedures were used in studies with B_{12} complexes, except that aquocobalamin (Sigma Chemical, St. Louis, Mo.) was mixed directly with Cr^{2+} to obtain vitamin B_{12r} in solution.

Results and Discussion

Kinetic data are collected in Table I for the reaction of $Co([14]dieneN_4)(NH_3)_2^{3+}$ with mixtures of Cr^{2+} and $Co^{II}([14]tetraeneN_4)$. The experimental rate law may be expressed as in (1) with $k' = 0.12 \pm 0.04\ M^{-1}\ s^{-1}$. The

$$-\frac{d[Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}]}{dt} = k'[Cr^{2+}][Co^{II}([14]tetraeneN_4)] \quad (1)$$

reaction system may be plausibly described by reactions 2–5.

$$Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+} + Cr^{2+} \xrightarrow[H_3O^+]{k_2} Co([14]\text{-}4,11\text{-}dieneN_4)(OH_2)_2^{2+} + 2NH_4^+ + Cr^{3+} \quad (2)$$

$$Co([14]tetraeneN_4)(OH_2)_2^{2+} + Cr^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co^I([14]tetraeneN_4) + Cr^{3+} \quad (3)$$

$$Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+} + Co^I([14]tetraeneN_4) \xrightarrow[H_3O^+]{k_4} Co([14]\text{-}4,11\text{-}dieneN_4)(OH_2)_2^{2+} + 2NH_4^+ + Co([14]tetraene)(OH_2)_2^{2+} \quad (4)$$

$$Co^I([14]tetraeneN_4) + H^+ \xrightarrow{k_5} HCo([14]tetraeneN_4)^{2+} \quad (5)$$

This reaction scheme, assuming a stationary state in $Co^I([14]tetraeneN_4)$, leads to the rate expression in eq 6, provided

$$-\frac{d[Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}]}{dt} = \frac{k_3k_4[Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}][Cr^{2+}] \times [Co([14]tetraeneN_4)(OH_2)_2^{2+}]}{k_{-3}[Cr^{3+}] + k_4[Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}] + k_5[H^+]} \quad (6)$$

$k_2[Cr^{2+}][Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}] \ll$ rate as given

Table I. Kinetic Data for the Co^{II}([14]tetraeneN_4)-Catalyzed Cr^{2+} Reduction of Co([14]dieneN_4)$(NH_3)_2^{3+}$ [a]

10^{-5}[Co([14]-dieneN_4)-$(NH_3)_2^{3+}$], M	10^{-5}[Co^{II}([14]-tetraeneN_4)], M	10^{-2}[Cr^{2+}], M	10^{-3}[Cr^{3+}], M	[H^+], M	Apparent zero-order rate × 10^{-6}, M s^{-1}	$10^{-1}k'$, M^{-1} s^{-1}
4.12	16.5	7.0	1.09	10^{-1}	1.3	1.1
8.25					1.4	1.2
1.24					1.3	1.1
1.64					1.4	1.2
8.25	4.12	2.2			0.13	1.4
	8.25				0.22	1.2
	12.4				0.33	1.1
	16.5				0.41	1.1
	41.2				1.2	1.3
	16.5	0.91			0.18	1.2
		2.18			0.41	1.1
		3.48			0.80	1.4
		4.36			0.65	0.90
		7.00			1.4	1.2
			10.9		1.5	1.3
			22.0		1.4	1.2
			1.09	0.5	1.1	0.95
				10^{-2}	1.6	1.4
				10^{-3}	1.6	1.3

[a] Ionic strength 0.82 M ($HClO_4$, $NaClO_4$); $T = 25$ °C. No entry is made for reagent concentrations if the concentration is the same as in the preceding entry for that reagent.

by (6). Our previous study[2] has shown $k_2 = 4.0 \times 10^{-3}$ M^{-1} s^{-1} so $k_2 \ll k'$ and the condition is easily met. The observed rate law, (1), requires that k_4[Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$] > $\{k_{-3}[Cr^{3+}] + k_5[H^+]\}$. The reversible electrochemical reduction of Co([14]tetraeneN_4)$(OH_2)_2^{2+}$ occurs with $E_{1/2} = -0.72$ V vs. SCE in 0.1 M $NaClO_4$ (Figure 1), so $E° \simeq -0.5$ V for the Co^{II}([14]tetraene)–Co^{I}([14]tetraene) couple; from this we may estimate $K_3 \approx 3 \times 10^{-2}$ and $k_{-3} \approx 4$ M^{-1} s^{-1}. Thus under our conditions $k_{-3}[Cr^{3+}] \leq 0.08$ s^{-1} and does not appear to make a significant contribution.

The apparent zero-order dependence of the rate on the concentration of cobalt(III) substrate over the range of conditions reported in Table I indicates that at the extremes less than 30% of the cobalt(I) intermediate can be consumed by reaction 5 when [Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$] = 1.24×10^{-5} M and [H^+] = 0.10 M; i.e., $k_4 \gtrsim 2.4 \times 10^4 k_5$. Tait et al.[4] have reported that $k_5 = 1.6 \times 10^5$ M^{-1} s^{-1} at ionic strengths between 0.06 and 0.6 M. To be consistent with this report, the reactions proposed would require that $k_4 \geq 3.8 \times 10^9$ M^{-1} s^{-1} at an ionic strength of 0.8 M. Given that Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$ tends to be significantly more reactive than $Co(NH_3)_6^{3+}$ [2] and that the cobalt(I) species are exceptionally facile reductants,[4] a diffusion-limited value for k_4 is not unreasonable, so the two studies are not necessarily inconsistent and k' may be identified with k_3.

We have performed a few experiments which indicate that aquocobalamin can function in a manner similar to Co([14]tetraeneN_4)$(OH_2)_2^{2+}$ in the Cr^{2+}–Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$ reaction. However our attempts to quantitate the similarities were frustrated by a relatively more favorable competition of H^+ for the reactive intermediate. The sensitivity of Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$ to base hydrolysis[8] made a pH of 3.5 the practical upper limit in these studies, and the rate of the catalyzed reaction was significantly inhibited by acid at all pH values ≤3. We did find the rate law to be approximately zero order in [Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$] at pH 3.5 but first order in the cobalt(III) substrate at pH 1.

We have made extensive attempts to generate aqueous solutions of Co^{I}([14]tetraeneN_4) by electrolytic reductions. These attempts resulted in the formation of powerfully reducing blue solutions, solutions capable of generating H_2 when acidified and having absorption spectra not significantly different from those reported by Tait et al.[4] for Co^{I}([14]-tetraeneN_4). However, the electrolyzed solutions always had pH >10 and very similar species are generated in deaerated basic solutions of Co([14]tetraeneN_4)$(OH_2)_2^{2+}$.[9] Furthermore, the blue reducing complexes were far less reactive toward H^+ than Tait et al.[4] reported for Co^{I}([14]tetraeneN_4).

We have also observed that Co([14]tetraeneN_4)$(OH_2)_2^{2+}$ is unstable in strongly acidic ([H^+] ≥ 1 M) solutions concentrated in Cr^{2+} (≥0.1 M). In such solutions, the [Co([14]tetraeneN_4)$(OH_2)_2^{2+}$] decreases very slowly (k_{app} of the order of 10^{-1}–10^{-2} M^{-1} s^{-1}), presumably owing to the decomposition reactions of "HCo([14]tetraeneN_4)$^{2+}$". There was no evidence for gaseous products and the only product absorbing in the visible region appeared to be Cr^{3+}.[11]

Conclusions

We have elsewhere noted that the Cr^{2+} reduction of Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$ is exceptionally slow apparently owing to a combination of unfavorable Franck–Condon reorganizational and orbital overlap factors in the transition-state combination of the two reactant partners.[2,12] Given that reactant combinations exist for which the apparent reorganizational parameters are very small,[6b,12a] then catalytic pathways can be found provided the obvious thermodynamic restrictions are met. If we express this in the formulation due to Marcus,[13] then a substance X can act as an electron-transfer catalyst in outer-sphere reactions provided the apparent reorganizational parameters stand in the relation ($\lambda_{Cr} + \lambda_{Co}$) > ($\lambda'_{Cr} + \lambda'_{Co} + 2\lambda_X$), where ($\lambda_{Cr} + \lambda_{Co}$) are the appropriate reorganizational parameters for (2), ($\lambda'_{Cr} + \lambda_X$) for (3), and ($\lambda'_{Co} + \lambda_X$) for (4).[14] This relation can only hold if ($\lambda_{Cr} + \lambda_{Co}$) > ($\lambda'_{Cr} + \lambda'_{Co}$) and the catalytic effect dramatizes the anomalous behavior of reorganizational parameters for reactant couples involving one member with one $^*\sigma_M$ orbital singly occupied and the other member with vacant $^*\sigma_M$ orbitals. In contrast it is to be noted that while the cobalt(II)–cobalt(I) couple is d^7–d^8, therefore involving change of electron density in $^*\sigma_M$ orbitals, the observation of a catalytic effect requires λ_X to be small presumably because large axial distortions occur in both the oxidized and reduced species.[12b,12c,15]

Registry No. Co^{II}([14]tetraeneN_4), 58815-31-9; Co([14]-dieneN_4)$(NH_3)_2^{3+}$, 36452-44-5; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Figures 2 and 3 relating observed acid decomposition of the species obtained from electrolytic reductions of Co^{II}([14]tetraene) (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged. (b) Presented in part at the 163d National Meeting of the American Chemical Society, New York, N.Y., Aug 1972.

(2) D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, **11**, 2361 (1972).

(3) Abbreviations for the macrocyclic ligands: [14]tetraeneN_4, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; [14]dieneN_4, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

(4) A. M. Tait, M. Z. Hoffman, and E. Hayon, *J. Am. Chem. Soc.*, **98**, 86 (1976).

(5) D. P. Rillema and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 8711 (1972).

(6) (a) M. P. Liteplo and J. F. Endicott, *Inorg. Chem.*, **10**, 1420 (1971); (b) D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Am. Chem. Soc.*, **94**, 394 (1972).

(7) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).

(8) D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).

(9) B. Durham and J. F. Endicott, work in progress.

(10) For example we found half-lives of the order of 7 s in the "Co^Itetraene" solution about 10^{-4} M in reductant at pH 4 (see supplementary material), where Tait et al.[4] would predict a 0.06-s half-life for (5) under these conditions. It should be noted that these reducing solutions appeared to be stoichiometrically oxidized by various species including $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}$ with apparent second-order rate constants of about 6×10^3, 3×10^2, and 1.4×10^5 $M^{-1}\ s^{-1}$, respectively (ionic strength 0.1 M, 25 °C).

(11) We wish to thank Dr. C. Y. Mok for assistance with these experiments.

(12) (a) J. F. Endicott, R. R. Schroeder, D. H. Chidester, and D. R. Ferrier, *J. Phys. Chem.*, **77**, 2579 (1973); (b) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Am. Chem. Soc.*, **95**, 5097 (1973); (c) M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *ibid.*, **96**, 5661 (1974).

(13) (a) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); (b) *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

(14) These expressions may be obtained as follows: for (2), $\Delta G^{\ddagger}_{Cr,Co} \simeq 1/8(\lambda_{Cr} + \lambda_{Co}) + \Delta G^{\circ}_2/2 + \ldots$; for (3), $\Delta G^{\ddagger}_{Cr,X} \simeq 1/8(\lambda'_{Cr} + \lambda_X) + \Delta G^{\circ}_3/2 + \ldots$; for (4), $\Delta G^{\ddagger}_{X,Co} \simeq 1/8(\lambda_X + \lambda'_{Co}) + \Delta G^{\circ}_4 + \ldots$. The reorganizational parameters are defined with regard to the reactions specified with the exception that we have assumed a single value for λ_X; i.e., since λ_X must be relatively small for the catalytic pathways, small differences between λ'_X for oxidation of $Co^I([14]tetraeneN_4)$ and λ''_X for reduction of $Co^{II}([14]tetraeneN_4)$ may be ignored. Owing to the similar half-reactions involved, $\Delta G^{\circ}_2 - \Delta G^{\circ}_3 - \Delta G^{\circ}_4 = 0$, so we may consider $\Delta G^{\ddagger}_{Cr,Co} - \Delta G^{\ddagger}_{Cr,X} - \Delta G^{\ddagger}_{X,Co} \simeq 1/8[(\lambda_{Cr} + \lambda_{Co}) - (\lambda'_{Cr} + \lambda'_{Co} + 2\lambda_X)] = \Delta\Delta G^{\ddagger}$. In order for the catalytic pathway to be significant, $\Delta\Delta G^{\ddagger} > 0$; hence we have the expression in the text.

(15) While the d^7 complexes are axially distorted in the solid state,[12b,12c] the d^8 nickel(II) analogues tend to be square planar, perhaps owing to somewhat weaker axial interactions. For examples see: (a) M. F. Bailey and I. E. Maxwell, *Chem. Commum.*, 883 (1966); (b) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1966).

Contribution from the Department of Chemistry,
University of Maine, Orono, Maine 04473

Isotopic Splitting in the Sharp-Line Luminescence Spectrum of the Tetrachloroplatinate(II) Ion at 4 K

Howard H. Patterson,* Thomas G. Harrison,
and Robert J. Belair

Received October 1, 1975 AIC507209

In 1972 Patterson, Godfrey, and Khan[1] reported sharp-line luminescence and absorption spectra for the tetrachloroplatinate(II) ion doped in the host lattice of cesium hexachlorozirconate(IV) at 4 K. In particular, the sharp-line luminescence occurred between 19 450 and 23 190 cm^{-1} and consisted of more than 30 distinct emission lines. Group theoretical analysis of the sharp emission lines showed that the emitting excited electronic state could only be of a certain symmetry. Also, Franck–Condon analysis showed that the Pt–Cl equilibrium separation in the excited emitting electronic state is 0.16 Å greater than in the ground state. It was argued that the reason for the splitting in the E and O peaks was that as transitions occur into the ground electronic state with more quanta of the ν_1 symmetric stretch mode excited, the complex samples to a greater extent its surroundings, and ions with slightly less than cubic site symmetry give rise to additional peaks. In this paper a different explanation is proposed for the splittings.

Table I. Energies of E and O Peak Components for $PtCl_4^{2-}$ Luminescence Spectrum

n value	O peak component no.	Energy, cm^{-1}	E peak component no.	Energy, cm^{-1}
0			$10E_1$	22 358
1	$8O_1$	21 888	$9E_1$	22 022
			$9E_2$	22 030
2	$7O_1$	21 560	$8E_1$	21 700
	$7O_2$	21 565	$8E_2$	21 705
			$8E_4$	21 725
3	$6O_1$	21 230	$7E_1$	21 371
	$6O_2$	21 236	$7E_2$	21 379
	$6O_3$	21 245	$7E_3$	21 385
			$7E_4$	21 396
			$7E_5$	21 403
4	$5O_1$	20 902	$6E_1$	21 041
	$5O_2$	20 911	$6E_2$	21 049
	$5O_3$	20 921	$6E_3$	21 059
			$6E_4$	21 070
5	$4O_1$	20 576	$5E_1$	20 714
	$4O_2$	20 587	$5E_2$	20 724
	$4O_3$	20 598	$5E_3$	20 736
			$5E_4$	20 748
6	$3O_1$	20 252	$4E_1$	20 389
	$3O_2$	20 263	$4E_2$	20 401
	$3O_3$	20 277	$4E_3$	20 414
			$4E_4$	20 425
7	$2O_1$	19 924	$3E_1$	20 061
	$2O_2$	19 939	$3E_2$	20 076
			$3E_3$	20 093
			$3E_4$	20 107
8			$2E_1$	19 734
			$2E_2$	19 751
			$2E_3$	19 768
9			$1E_1$	19 403
			$1E_2$	19 422

The purpose of this paper is to demonstrate that the sharp splittings in the luminescence spectrum are due to the presence of ^{35}Cl and ^{37}Cl isotopes in the emitting tetrachloroplatinate(II) ion. The analysis is not dependent upon any adjustable parameters. Further, the analysis is different if the emitting species is Pt(IV) rather than Pt(II) and provides further evidence that the emitting species is indeed $PtCl_4^{2-}$ rather than $PtCl_6^{-2}$. As far as we are aware, there have been few reports of vibrational isotopic splitting observed in electronic spectra for inorganic compounds;[2-4] however, this effect is well-known in Raman and infrared vibrational spectra.

Results

In the top portion of Figure 1, the luminescence spectrum of a Cs_2PtCl_4–$CsZrCl_6$ single crystal at a temperature of 4 K is shown. The details of the spectroscopic measurements have been given previously in ref 1.

The Figure 1 spectrum contains two sets of peaks labeled E and O, with the E peaks having greater relative intensity than the O peaks. The progression of E peaks extends from 19 406 to 22 500 cm^{-1} with an intensity maximum around 21 000 cm^{-1}. In contrast, the O peak progression is very similar to the E peak progression except that the O peaks seem to extend to about 23 500 cm^{-1}. However, if the O peak progression is carefully examined, it is found that peak 9O is broad and does not have the same general appearance as the other O peaks. Also, if the O peak splitting is measured as a function of increasing energy, it is found that the O peak splitting continually decreases until 9O, increases at 9O, and