cam)$_3$ appears to be sufficient in size to accommodate quite large nucleophiles.

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Supplementary Material Available. Table I, atomic coordinates in (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-1586.

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Excitons in One-Dimensional Tetracyanoplatinite Salts

Sir:

Although the recent flurry of activity[1] on the electronic properties of metal chain compounds has been mainly concerned with the so-called "partly oxidized" (i.e., mixed valence[2]) platinum salts, in the solid state quite a lot of ordinary divalent square planar platinum salts form stacks in which the metal atoms are also brought into reasonably close proximity. These compounds are of course insulators, not metals, but they do have extremely unusual optical properties which are clearly the result of the one-dimensional character of their crystal lattices. The purpose of this note is to draw attention to a strikingly simple correlation between the structural and optical parameters in one set of Pt(II) salts, the tetracyanoplatinites, which strongly suggests that the lowest excited states of one-dimensional single valence platinum compounds can be described as neutral Frenkel excitons, propagating along the stacks.

Briefly stated, the unusual optical properties of the tetracyanoplatinites are the following: in dilute aqueous solution the isolated $Pt(CN)_4{}^{2-}$ ion has major absorption bands at 35,800 (ϵ = 1480), 39,200 (ϵ = 10700), and 46,100 cm^{-1} (ϵ = 22100).[3] It does not appear to have any further absorption bands, even weak ones, at lower energies. Nevertheless, many tetracyanoplatinite salts, particularly those of group 1A and 2A cations are intensely colored and, moreover, exhibit strong visible luminescence. Polarized single-crystal reflection spectra[4] of Mg, Ca, Sr, and Ba tetracyanoplatinites demonstrate that at room temperature the visible absorption consists of a single broad band, polarized almost entirely parallel to the metal atom chains, whose oscillator strength in that direction has the order of magnitude of unity. The frequency of the band varies very markedly from one salt to another; it lies lowest in $MgPt(CN)_4 \cdot 7H_2O$, which also has the shortest Pt–Pt spacing (3.13 Å[5]). That the frequency in fact varies monotonically with Pt–Pt spacing is demonstrated by the extensive set of structural and optical data collected by Moreau-Colin.[6]

Since the tetracyanoplatinites are insulating crystals in which the molecular units remain clearly distinguishable, it seems a priori probable that the lowest crystal excited states should be neutral Frenkel excitons formed from simple molecular transitions, coupled by the intermolecular interaction potential. The simplest approximation to the latter is the point multipole expansion. Because the intense low energy crystal absorption band is polarized parallel to the Pt chains, its origin must lie in an allowed transition polarized perpendicular to the planes of the units, i.e., A_{2u} in the double group $D^*{}_{4h}$, which could arise either from a metal-to-ligand charge transfer ($d_{z^2} \rightarrow a_{2u}\pi^*$) or a $d_{z^2} \rightarrow p_z$ transition of the metal or, perhaps more likely, some admixture of the two. The molecular transition dipole vectors within each stack then being parallel to one another, the resulting crystal transition should suffer a Davydov shift to lower energy which in the point dipole approximation,[7] and assuming only interactions between nearest neighbors in the stack, would be $2e^2|M|^2/R^3$, where M is the transition dipole moment in the free ion and R is the Pt–Pt spacing within the stack. This possibility was mooted some years ago[8] but without definitive evidence.

An obvious means of testing whether the observed bands are indeed still Davydov components would thus be to plot their energies against R^{-3}. This we have done in Figure 1, for both tetracyanoplatinites and tetracyanopalladites, using the data of Moreau-Colin.[6] The result is such an excellent linear correlation that there can be no doubt of the essential correctness of the original hypothesis. Furthermore the extrapolated frequencies of the transitions at $R = \infty$ (i.e., for the free ions) are 44,800 and 52,900 cm^{-1} for $Pt(CN)_4{}^{2-}$ and $Pd(CN)_4{}^{2-}$, respectively, well within the range of energy of the intense transitions of both ions in solution.

Yet more confirmation comes from the assignments of the relevant states in the free ions. A spin-orbit calculation[3]

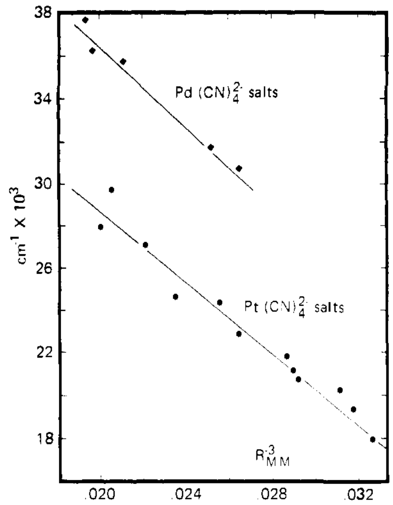

Figure 1. Absorption energies and nearest neighbor metal–metal distances in tetracyanoplatinites and tetracyanopalladites.

carried out to assign the solution magnetic circular dichroism spectrum of $Pt(CN)_4{}^{2-}$ placed the A_{2u} state with predominant $^1A_{2u}$ parentage beneath the band envelope at 46,100 cm^{-1}, while a transition state calculation[9] of the $5a_{1g} \rightarrow 3a_{2u}$ ($^1A_{2u}$) excitation in the same ion by the Xα scattered wave method predicted it at 50,600 cm^{-1}. Bearing in mind that the reference point of the Davydov calculation is the free ion in the gas phase, the agreement of these numbers with the extrapolated free ion excitation energy is satisfactory. Turning to the intensity in the simple point dipole approximation, the slope of the line in Figure 1 would be just $-2e^2|M|^2$; experimentally it is approximately $-0.008e^2A^2$, equivalent to a transition dipole length of about 1.9 Å. An estimate based on the area of the 46,100-cm^{-1} absorption band of $Pt(CN)_4{}^{2-}$ in solution was just under 0.8 Å. This discrepancy between the observed and predicted free ion dipole lengths is no doubt a measure of the approximation we have made by assuming only a point dipole–dipole interaction and not carrying out a summation over the whole lattice. Nevertheless, the discrepancy is not too great.

The success of this extremely simple approach to the tetracyanoplatinite crystal spectra leads us to suggest that the unusual optical properties of other crystals containing one-dimensional arrays of square planar d^8 complexes, such as the dimethylglyoximates,[10] might be capable of a similar explanation, as we already tentatively suggested earlier.[11]

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Radical Ions of Benzene and Toluene in Nonpolar Solvents

Sir:

We report the preparation, through use of a crown ether, of the radical anions of benzene and toluene in nonpolar solvents. The simplest preparation is carried out by bringing a solution of dicyclohexyl-18-crown-6 in the parent hydrocarbon into contact with a potassium mirror. A reaction occurs, complete in a few hours at room temperature, after which the electron spin resonance spectrum of the anion is observed. The manipulations are carried out under high vacuum.

The benzene anion thus prepared in solution in benzene has a proton hyperfine coupling constant of 3.41 G. No deviation from equivalence of the six protons is observed. The spectrum is not as well resolved as in ethereal solvents at low temperature, being simulated by assignment of breadth 1.30 G between points of extreme slope to each of the seven lines. A Lorentzian shape, undistorted by unresolved hyperfine splitting, was used in the simulation.

The toluene anion is prepared just as is the benzene anion. The dominant feature of its spectrum is hyperfine splitting by four equivalent protons with a coupling constant of 4.5 G. There is a suggestion, most apparent on the component at lowest field, of further splitting of 0.7 G by coupling to the potassium counterion.

In both the benzene and toluene ions the proton hyperfine couplings are significantly smaller than in solution in ethers, about 10% in benzene and 20% in toluene.

The most surprising feature of the spectra is that in the pure parent hydrocarbon solvent the electron transfer between anion and solvent molecules does not wash out the hyperfine splitting. If the entire line breadth of the benzene anion arose from electron transfer, the second-order rate constant for the process could be no greater than 7×10^6 M^{-1} sec^{-1}.

Since the electron spin resonance spectra of the radical ions are almost completely resolved, the rate of electron transfer may be determined directly from the broadening of the proton magnetic resonance lines of the solvent. Determination of the rate constant requires knowledge of the concentration of radical anion. In one set of experiments we started with a solution of the crown ether at 1.5×10^{-2} M, presumably the stoichiometric maximum concentration of benzene anion which could be produced in that solution. The electron spin resonance of the resulting anion displays marked broadening owing to Heisenberg exchange. Since Heisenberg exchange rates are close to the encounter controlled limit,[1,2] we made an independent estimate of the radical concentration by matching the observed spectrum to one calculated for benzene anion undergoing Heisenberg exchange. Assumption that the Heisenberg exchange rate constant is 2×10^9 M^{-1} sec^{-1} leads to an estimated anion concentration of 0.7×10^{-2} M. Lacking an absolute spin count, we assume that the concentration of radical anion was between 0.7×10^{-2} M and the stoichiometric upper limit of 1.5×10^{-2} M. The proton magnetic resonance of the benzene in solution has full width at half maximum of 520 Hz. The rate constant for electron transfer, at the temperature at which the proton magnetic resonance was observed, is estimated to be between 1.0×10^5 and 2×10^5 M^{-1} sec^{-1}.

Similar results with a rate constant of the same order are obtained with toluene. As expected, the methyl proton lines are not as broad as those of the four-ring protons because their small hyperfine constants are of the same order as the reciprocal residence time of the electron spin on a toluene molecule. Consequently the simple strong pulse limit equa-