Review

Solid-state spectral perturbations in square-planar complexes

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Dedicated to Edward Solomon

Abstract

A brief overview of color changes of square-planar complexes upon crystallization is presented along with selected spectra and theoretical spectral modeling results. In general, brilliant colored crystals of several square-planar complexes develop from colorless solution. The systems include Magnus' green salt, tetracyanometallates, and bis(dimethylglyoximato)nickel(II). It is generally accepted that the transition responsible for a spectral red shift and increase in intensity is from an uppermost filled orbital with a large metal d_{z^2} component to a low-lying empty metal-based p_z orbital. Since these orbitals are largely oriented out of plane, they interact most strongly when the planes are aggregated. Experimental data from selected single-crystal polarized specular reflectance spectra and ZINDO calculations on several systems are reviewed.
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Ronald L. Musselman *received his Ph.D. in Physical Chemistry from New Mexico State University in 1971 and began his teaching career at Principia College in Elsah, Illinois. While there he became Professor of Chemistry and was a visiting scholar with Prof. Edward I. Solomon at Stanford University, Prof. Steven Watkins at Louisiana State University and Dr. Jack Williams at Argonne National Laboratory. His next position was at Franklin and Marshall College in Lancaster, Pennsylvania where he was also Professor of Chemistry. He is now Research Professor in Chemistry at the University of South Florida in Tampa, Florida. Prof. Musselman is recognized as an expert in solid-state UV/vis spectroscopy, specifically, polarized specular reflectance spectroscopy. His research tools include, in addition to reflectance spectroscopy, X-ray structural studies and ZINDO and ab-initio solid-state calculations. His current areas of interest include energy-transforming new materials including porphyrin-Fullerenes, biologically relevant porphyrin derivatives and solid-state electronic properties of pharmacologically active materials.*

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1. Introduction

Solid-state spectral perturbations, sometimes known as solid-state effects, where colored crystals form from colorless solutions or the color of a crystal changes with pressure have been long known in planar tetracyanometallates, metal complexes of glyoximes and other planar complexes such as Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$ and Vauquelin's red salt, $[Pd(NH_3)_4][PdCl_4]$ [1–13]. The effect need not be limited to changes in visible spectra, of course, but the visible changes draw the most attention. Such solid-state perturbations are of interest because they are due to non-localized interactions between molecules in the solid state and have broad implications in solid-state semiconducting and energy-transforming materials [14–19]. We plan to present a brief background of the phenomenon in several square-planar complexes and to review the spectra and modeling calculations on some of the examples.

Tetracyanoplatinates show brilliant color changes which depend upon the stacking distance between $Pt(CN)_4^{2-}$ planes [20–22]; this is illustrated in Fig. 1. Another example is the red color of $Ni(dmg)_2$ found in the quantitative determination of nickel, a test that is now over 100 years old [23–25]. Color change is in some cases associated with semi-conductivity [14,15,26,27] which requires some degree of delocalization of electrons in a solid. The transition responsible for the brilliant color has been shown to be polarized in
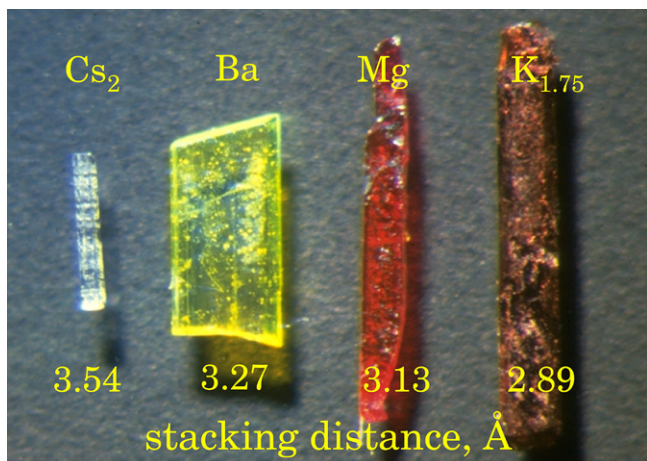

Fig. 1. Single crystals of several tetracyanoplatinates showing a color change with a change in stacking distance. The Pt in the $K_{1.75}$ salt is partially oxidized and exhibits metallic reflectance.

the out of plane direction and its intensity is usually much larger than in an unperturbed state [2,3,11,28–32]. The traditional explanation of the phenomenon is that a single-molecule $d_{z^2} \rightarrow p_x$, π^* transition in the UV becomes sufficiently lower in energy to appear in the visible in the solid state. In addition, the orbitals involved in the transition overlap more in the solid state than in the single molecule, thus effecting a stronger transition than in the unperturbed case.

In this paper, we will review some of the experimental evidence of the solid-state effect, emphasizing tetracyano and dimethylglyoxime complexes, and discuss some calculations that have clarified the causes of the effect. Since the phenomenon is a solid-state one and we are looking at spectra, we will review the technique we and other labs [29,33,34] have used to study the UV/vis spectra of solids: polarized specular reflectance spectroscopy. We will also briefly review the use of a simple yet surprisingly successful calculation technique for the interpretation of the solid-state perturbations: ZINDO (Zerner's modification of Intermediate Neglect of Differential Overlap).

2. Experimental

2.1. Specular reflectance

The transitions of interest in this review are those where the transition moment integral,

$$Q = \int \Psi_e |\mathbf{r}| \Psi_g d\tau, \tag{1}$$

is formally non-zero, that is, where the combined symmetry of the ground state, perturbing operator, and excited state is the totally symmetric member of the point group of the system at hand. For example, in a D_{4h} system, the integrand would need to have a direct product of A_{1g}.[1] This typically results in an absorbance coefficient, epsilon, of between 1000 and 100,000 $M^{-1} cm^{-1}$. Since we are studying solids, we of course need to measure the absorbance of the condensed material and an epsilon of 100,000 $M^{-1} cm^{-1}$ would require a path-length of about 5×10^{-3} mm. Since this would be difficult to work with experimentally, it is easier to use natural crystals and take advantage

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[1] In the case of degenerate components, several irreducible representations would result upon reducing the direct product, but only one of them needs to transform as A_{1g}.