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Absorption Spectrum of Magnus' Green Salt in the Near-Infrared Region

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Received November 24, 1971

The planar complex ions in Magnus' green salt (MGS), $[Pt(NH_3)_4][PtCl_4]$, are arranged in columnar stacks in the solid, giving rise to linear chains of platinum atoms with a uniform metal–metal separation of 3.25 Å.[2] The absorption spectrum of this compound in the near-infrared region has been a subject of considerable interest and controversy in recent years.

Early work, employing diffuse reflectance measurements and transmission spectra of KCl disk samples, indicated a strong, broad absorption band in this region centered at ~6.0 kK and extending over several thousand reciprocal centimeters, which could not be accounted for in terms of transitions localized on the individual ions in MGS.[3] The absorption was subsequently ascribed to intermolecular transitions in the solid and a qualitative band description proposed to account for its apparent broad, intense character. This band description, which presumes that the only bands of significant width are those which arise from interactions of the d_{z^2} and p_z orbitals on the platinum atoms, has been extensively used in accounting for the results of subsequent studies of the electrical properties of MGS and other complexes of this structural type.[4] In the case of MGS, the semiconductivity behavior and the photoconductivity response observed in the near-infrared region were attributed to electronic transitions across a forbidden "$d_{z^2} \rightarrow p_z$ band gap" in the solid. This band gap was assumed to be on the order of 0.6 eV on the basis of the measured thermal activation energy for conductivity as well as the spectral and photoconductivity observations.

Later spectral studies on single crystals of MGS[5] and an estimate of the $d_{z^2} \rightarrow p_z$ band gap obtained from semiempirical band structure calculations[6] have raised considerable doubt regarding the character of this near-infrared absorption and its assignment. Moreover, recent single crystal conductivity measurements have shown that impurity effects can be of considerable importance in determining the electrical conductivity of this compound, thus bringing into serious question the intrinsic band model upon which the assignment is based.[7]

In an attempt to answer the questions regarding the absorption spectrum in this region raised by previous work, we have undertaken a reexamination of the spectrum between 2.8 and 12 kK, the results of which are reported herein.

Experimental Section

The spectroscopic work in the region from 12 to 4.0 kK was performed using a Beckman DK II spectrophotometer equipped with a beam condenser. The automatically controlled slit widths ranged from 0.3 to 0.1 mm due to the use of low transmission screens in the reference beam (3–17% transmittance). For a few experiments reported utilizing single beam optics, a Perkin-Elmer Model 98 spectrophotometer was used with a "Quartz-line" lamp source, an external focus for the sample, and a lead sulfide detector. A Perkin-Elmer Model 521 infrared spectrophotometer with a beam condenser was used in the region from 4.0 to 2.8 kK.

Most of the single crystal samples used were prepared by the gel diffusion technique.[7,8] These crystals were optically clear and had well-formed faces at right angles to one another. They ranged in length from ~0.5 to 2 mm, in width from ~0.2 to 0.5 mm and in thickness from ~0.02 to 0.2 mm. The crystals were mounted over a slit cut in thin nickel foil and held in place with a dab of silicone stopcock grease at each end. The spectra obtained using crystals of widely varying thickness with different per cent transmittance screens in the reference beam were, in general, well defined and were quite reproducible in terms of both the band positions and intensities.

It was found that the hydrogen in tetraammineplatinum(II) chloride exchanged readily with D_2O; hence deuterated MGS crystals were prepared by preliminary exchange and recrystallization of $Pt(NH_3)_4Cl_2 \cdot H_2O$ followed by crystal growth in D_2O. Here a frit diffusion technique was used, with D_2O between two frits and $Pt(ND_3)_4Cl_2$ and K_2PtCl_4, each dissolved in D_2O, on either side. This method did not yield as high quality crystals as the gel diffusion method, but proved to be the most feasible method for obtaining fully deuterated single crystals.

Results and Discussion

Preliminary experiments were carried out on polycrystalline samples of MGS using KCl disk and Nujol mull sampling techniques. These experiments indicated an apparent strong, very broad absorption band in the near-infrared; however, the position and character of this band were found to be quite variable, depending upon the nature of the scatter plate used in the reference beam. This extreme variability and the results of our single crystal studies indicate that this absorption is not the result of any transition in the crystal but that it arises from differences in light scattering between the sample and reference. It appears likely that the "strong" band observed in the previous diffuse reflectance measurements on this compound has a similar origin.

Earlier studies on single crystals of MGS have resulted in the complete assignment of the spectrum in the visible and near-ultraviolet regions in terms of transitions mainly localized on the $PtCl_4^{2-}$ ions.[5,9,10] Many of these transitions apparently have been shifted to lower energies relative to those in the free $PtCl_4^{2-}$ ion due to electronic interactions with the $Pt(NH_3)_4^{2+}$ groups in the solid. These studies did not include a detailed examination of the near-infrared spectrum; however, a very weak absorption band was noted at 7.5 kK, which was suggested to be an overtone of an N–H vibration, although apparently no direct evidence for

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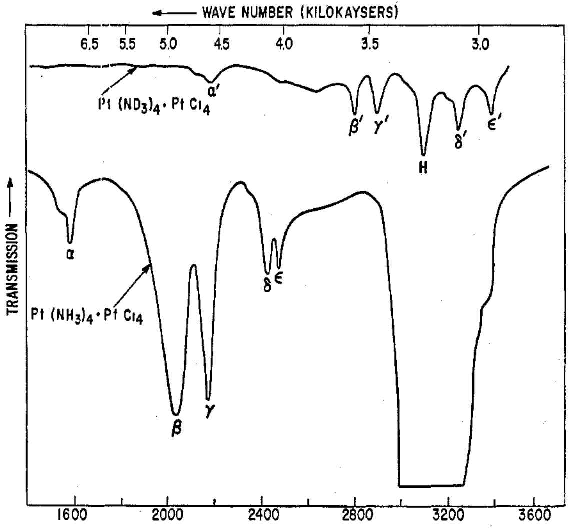

Figure 1.—Near-infrared spectra of crystals of $Pt(NH_3)_4PtCl_4$ and $Pt(ND_3)_4PtCl_4$. Corresponding bands are indicated by Greek letters, the primed letters referring to the deuterated case. The band labeled H is assigned to the fundamental N–H stretching vibration due to residual hydrogen.

this assignment has been reported.[5] In our experiments on single crystals of MGS using a double beam instrument, no absorption band was observed at 7.5 kK, although in single beam work on the same crystals an absorption which was attenuated upon purging with dry N_2 was noted at this position, indicating that its origin is the first overtone of the O–H stretching vibration of atmospheric water vapor.

Representative examples of the spectra obtained using the double beam instrument for both MGS and perdeuterio-MGS crystals are shown in Figure 1. In the case of the MGS crystals, six absorption bands were observed in the region between 12 and 2.8 kK, at 6.40, 4.85, 4.60, 4.12, 4.05, and 3.14 kK. The extinction coefficients of the first five bands ranged from 1 to 6 l./(mol cm). The much stronger band at 3.14 kK has been previously observed in infrared spectra of $Pt(NH_3)_4^{2+}$ salts[11] and is assigned to the NH_3 stretching fundamental. A band at this frequency also appears in the spectrum of the perdeuterio-MGS crystal and probably arises from residual hydrogen in the sample. The other five absorption bands all shift to lower energies in the spectrum of the deuterated crystal. The fractional shift (ν_D/ν_H) in each case was close to $1/\sqrt{2}$ (1/1.38, 1/1.32, 1/1.34, 1/1.33, and 1/1.37, respectively) indicating that they all arise as overtones and combinations of the NH_3 vibrations in $Pt(NH_3)_4^{2+}$. A qualitative survey of the infrared spectra of these same crystals down to 0.8 kK also failed to reveal any bands which could not be accounted for on the basis of vibrational transitions of the $Pt(NH_3)_4^{2+}$ ions.

In light of these observations, it is clear that the spectral properties of MGS in the near-infrared region and the results of the conductivity and photoconductivity measurements reported earlier[4] cannot be reconciled using the intrinsic band description previously presented for MGS.[8] This description presumes that the conductivity (σ) varies with temperature according to the relation, $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, where σ_0 is a preexponential term which varies only slowly with temperature and ΔE is the band gap.[12] Consequently, from measurements of σ *vs.* T and from photoconductivity studies, it should be possible to derive an estimate of the band-gap energy. These considerations and the appropriate experimental data lead to a value of $\sim$0.6 eV for the $d_{z^2} \rightarrow p_z$ gap.[4] Therefore, we would anticipate that the absorption edge for MGS should occur in the vicinity of 5 kK, resulting in strong absorption over a significant portion of the near-infrared. The absence of any absorption bands of electronic origin with $\epsilon > \sim 0.2$ l./(mol cm) in the entire region between 2.8 and 12 kK thus does not argue well for the applicability of the intrinsic model to MGS. On the other hand, the possibility of very weak ($\epsilon < \sim 0.2$ l./(mol cm)) absorption bands in this region, such as might arise from transitions involving impurities present in very small concentrations in the solid, cannot be excluded on the basis of the data obtained. As a result, a band description, suitably modified to include a small number of impurity levels within a few tenths of an electron volt of the d_{z^2} or p_z band edge and a band gap of >1 eV, remains as a possible alternative. Such an extrinsic band model would also account for the rather large impurity effects noted in a recent reexamination of the electrical conductivity of MGS.[7]

Acknowledgment.—This work was supported in part by the Air Force Office of Scientific Research, Air Force Systems Command, U. S. Air Force, under AFOSR Contract F44620-72-C-0006.

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The Linkage Isomerism of Bridging Thiocyanate in Binuclear Complexes

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Received December 14, 1971

Considerable interest has been shown recently in complexes containing the thiocyanate ligand because of its ability to coordinate through either the sulfur or nitrogen atoms. Infrared spectroscopy has been a valuable tool[2–4] in distinguishing between thiocyanato (M–SCN), isothiocyanato (M–NCS), and bridging (M–NCS–M) thiocyanato complexes.

While linkage isomerism of nonbridging thiocyanate complexes is well known,[5] including several instances in which the same molecule contains both metal–NCS

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