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BIS(PHTHALOCYANINATO) LANTHANIDE SANDWICH COMPOUNDS EXHIBITING MIXED VALENCE LIGANDS

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BIS(PHTHALOCYANINATO) LANTHANIDE SANDWICH COMPOUNDS EXHIBITING MIXED VALENCE LIGANDS

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ABSTRACT. Bis(phthalocyaninato) lanthanide sandwich compounds have been synthesized for ytterbium and thulium. Low temperature magnetic susceptibility data suggest a strong antiferromagnetic interaction between the lanthanide f-electrons and the phthalocyaninato ligand radical electron.

Introduction

Lanthanide sandwich compounds with the formula $Ln(Pc)_2$ have been known for over twenty-five years [1]. To a first approximation, the lanthanide ion has a formal oxidation state of +3, with one of the phthalocyanine ligands having a charge of -2, while the second phthalocyanine ligand is a singly oxidized radical with a charge of -1. The crystal structure of $[Lu(Pc)_2]\cdot CH_2Cl_2$ has been determined by Weiss et. al. [2] Other lanthanide sandwich compounds have essentially the same structure [3] in which the two phthalocyaninato rings are rotated an average of 45° with respect to one another, and it is assumed that the compounds described here have the same structure. Powdered samples of the compounds used in this study were verified by their ultraviolet, visible and near-infrared spectra and by elemental analysis. This paper will focus on the ytterbium and thulium bisphthalocyaninato sandwich compounds.

Experimental

Ultra-violet and visible spectra from 300 to 800 nm were collected on a Hewlett Packard Diode Array spectrophotometer at room temperature in CH_2Cl_2 solution. The near-infrared data from 750 to 1650 nm were collected

on a Cary-17 spectrophotometer at room temperature in CH_2Cl_2 solution. Magnetic susceptibility data of powdered samples were collected by using a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM) equipped with a Janis Research Co. liquid helium cryostat. The magnetometer was calibrated using $HgCo(NCS)_4$ [4]. Data were collected in the temperature range 4.2-120 K with a magnetic field of 1 kOe for Tm and 8 kOe for Yb. The data were corrected to compensate for the diamagnetism of the constituent atoms [5].

Results and Discussion

The ultraviolet, visible spectra of $Yb(Pc)_2$ and $Tm(Pc)_2$ show a Soret band at 320 nm and a Q band at 660 nm (figure 1) typical of phthalocyanine in its dianionic state [6]. The visible and near infrared spectra (figure 2) show a band at 458 nm (Yb) or 460 nm (Tm) and at 917 nm (Yb) or 915 nm (Tm), which correspond to the $2e_g(\pi) \rightarrow 1a_{1u}(\pi)$ and $1e_g(\pi) \rightarrow 1a_{1u}(\pi)$, respectively. These transitions are typical for phthalocyanine in its monoanionic state, due to the "missing" electron in the a_{1u} orbital [7]. The near infrared spectra also show a transition (figure 2) at 1386 nm (Yb) or at 1390 nm (Tm) which has been assigned to an intervalence charge transfer band [8], where the dianionic phthalocyanine acts as the donor and the monoanion acts as the acceptor.

Low temperature magnetic susceptibility data for these compounds reflect a strong antiferromagnetic interaction between the lanthanide f-electrons and the phthalocyaninato ligand radical electron. This antiferromagnetic coupling leads to a reduction of both the free ion spin multiplicity and the J-value of the free ion term. Normally, J is a good quantum number for most of the lanthanide ions [9] (except Eu and Sm), and large spin-orbit coupling causes J to J' separations which are much larger than the crystal field. In such cases, only the ground state is populated and the Landé g factor is given by:

$$g = 1 + [\{S(S+1) - L(L+1) + J(J+1)\}/\{2J(J+1)\}].$$

However, due to the coupling of the lanthanide f-electrons with the radical electron, two new states arise from the spin-orbit ground state (figure 3).

In the case of $Tm(Pc)_2$ the free ion ground state term symbol is $^3H_6$ and from the equation

$$\mu_{eff} = g\,[\,J(J+1)]^{1/2},$$

a limiting moment of 7.6 B.M. is expected. The experimental magnetic susceptibility data for $Tm(Pc)_2$ (figure 4) taken from 4.2 to 120 K appears to follow the Curie-Weiss law up to approximately 65 K where the moment

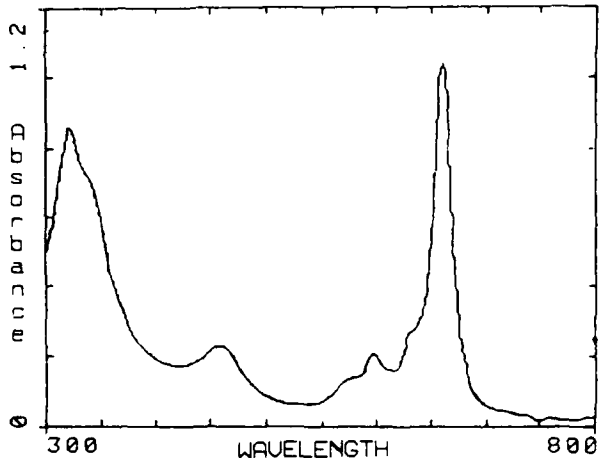

Figure 1: Ultraviolet and visible spectrum from 300 to 800 nm for $Tm(Pc)_2$ and $Yb(Pc)_2$ in CH_2Cl_2.

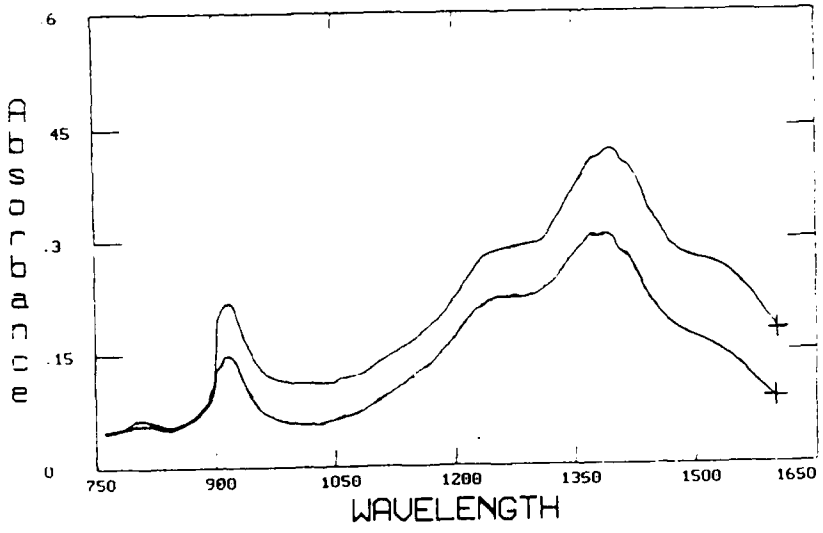

Figure 2: Near-infrared spectra for $Tm(Pc)_2$ (top) and $Yb(Pc)_2$ (bottom) from 750 to 1650 nm in CH_2Cl_2.

begins to level off at ~6.6 B.M. Above 65 K the susceptibility data appears to deviate from this behavior. The coupled terms which arise from the $^3H_6$ free ion ground term are a $^2H_{11/2}$ antiferromagnetically coupled term and a $^4H_{13/2}$ ferromagnetically coupled term. Initially assuming that only the $^2H_{11/2}$ state is populated, a Landé g-factor of 1.09 and a limiting moment of 6.5 B.M. is expected. An attempt to fit the data to the Curie-Weiss Law appears to model the data only up to ~65 K and gave a g value of 1.17 which gives only fair agreement with the theoretical value.

In the case of $Yb(Pc)_2$ the free ion ground state term symbol is $^2F_{7/2}$ and a limiting moment of 4.5 B.M. is expected. The experimental magnetic susceptibility data (figure 4) shows a leveling off of the moment of ~3.6 B.M. from ~ 30 to 55 K which again begins to show deviations from the Curie-Weiss law above 55 K. The coupled terms which arise from the $^2F_{7/2}$ free ion ground term (as shown in figure 3) are a $^1F_3$ antiferromagnetically coupled term and a $^3F_4$ ferromagnetically coupled term. Initially assuming that only the $^1F_3$ state is populated, a Landé g-factor of 1.00 is expected with a limiting moment of 3.5 B.M. An attempt to fit the data to the Curie-Weiss Law appears to model the data only up to ~55 K and gave a g value of 1.09 which also gives only fair agreement with the theoretical value.

It is apparent that this deviation from the Curie-Weiss Law is due to the presence of the low-lying higher spin multiplicity component arising from the exchange coupling. From the Van Vleck equation

$$\chi = \frac{N\sum_n \left[\frac{\left(E_n^{(1)}\right)^2}{kT} - 2E_n^{(2)} \right] \exp\left(\frac{-E_n^{(0)}}{kT}\right)}{\sum_n B_n \exp\left(\frac{-E_n^{(0)}}{kT}\right)}$$

when the energy of the antiferromagnetically coupled ground state $E_0^{(0)}$ is arbitrarily set equal to zero, the energy of the ferromagnetically coupled excited state $E_1^{(0)}$ is defined as ΔE, the first order zeeman energies are defines as $E_n^{(1)} = m_j g_j \beta$ and second order (and higher) effects are neglected, a simple expression can be derived to express the behavior of the magnetic susceptibility in these systems which is of the form:

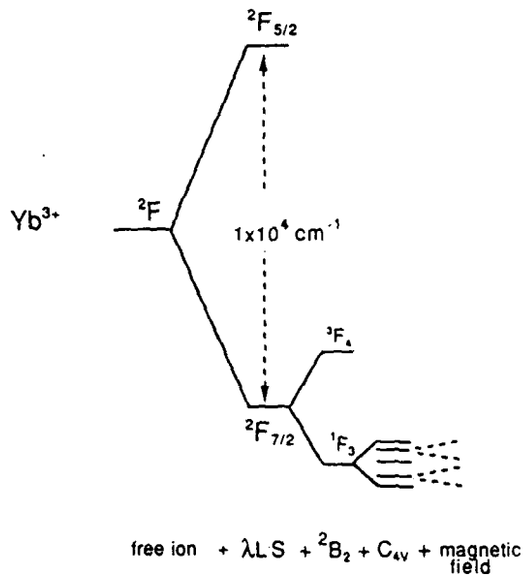

Figure 3: Schematic energy level diagram for the lanthanide, phthalocyaninato- radical coupled complex with ytterbium as the example.

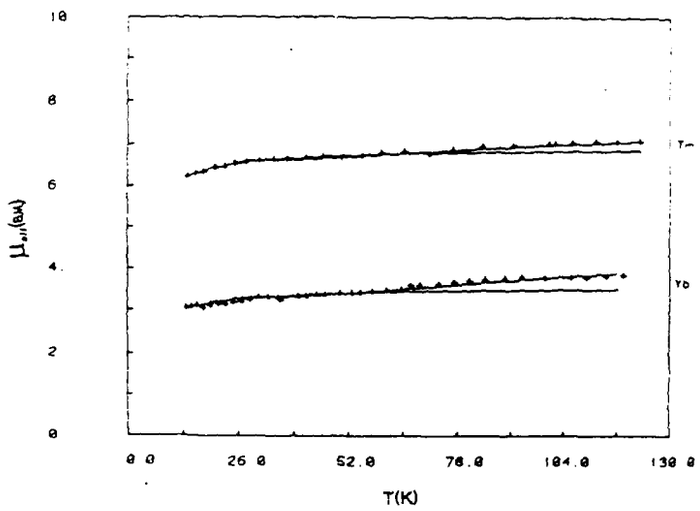

Figure 4: Magnetic susceptibility data for the bis(phthalocyaninato)-lanthanide(III) sandwich compounds. Experimental points are shown as +'s and best fit lines for the Curie-Weiss and VanVleck epressions are drawn (see text).

$$\chi = \frac{N\beta^2}{kT}\left\{\frac{\sum_j \left(m_{j_0} g_{j_0}\right)^2 + \sum_j \left(m_{j_1} g_{j_1}\right)^2 \exp\left(\frac{-\Delta E}{kT}\right)}{\left(2J_0+1\right) + \left(2J_1+1\right)\exp\left(\frac{-\Delta E}{kT}\right)}\right\}$$

When this equation, including the presence of both states, is fit to the data, excellent agreement is obtained for both the ground and excited states. For $Tm(Pc)_2$, $g(^2H_{11/2})_{calc} = 1.09$, $g(^2H_{11/2})_{exp} = 1.10$ and $g(^4H_{13/2})_{calc} = 1.23$, $g(^4H_{13/2})_{exp} = 1.21$ with a 106 cm^{-1} energy separation between states. Similarly, for $Yb(Pc)_2$, $g(^1F_3)_{calc} = 1.00$, $g(^1F_3)_{exp} = 0.95$ and $g(^3F_4)_{calc} = 1.25$, $g(^3F_4)_{exp} = 1.25$ with a 125 cm^{-1} energy separation between states.

In the figure of μ_{eff} vs. temperature (figure 4), the data points are shown as +'s. The solid lines drawn through the data points were generated by the Van Vleck equation with the parameters given above. The best fit Curie-Weiss lines are shown for comparison.

X-band EPR measurements from 0 to 8000 Oe at ambient and lower temperatures show no transitions at or near g=2, which would have been indicative of a free radical. The absence of a signal is due to the strong coupling between the phthalocyaninato ligand radical electron and the f-electron. At room temperature, both $Yb(Pc)_2$ and $Tm(Pc)_2$ are EPR silent. At 12.7 K, $Yb(Pc)_2$ shows two transitions at $g_1 = 4.34$ and $g_2 = 9.42$, while $Tm(Pc)_2$ at 7.2 K exhibits a very complicated spectrum with several transitions. The EPR spectrum of $Lu(Pc)_2$, which contains no unpaired f-electrons, exhibits the free radical transition at g = 2.00 at both 7.2 and 298 K.

It is apparent from the EPR spectra, reduction of the moment from the free ion value and excellent agreement of the experimental data with the Van Vleck model derived for these systems that a strong coupling exists between the phthalocyaninato ligand radical electron and the f-electrons for $Tm(Pc)_2$ and $Yb(Pc)_2$. It should be noted that $Yb(Pc)_2$ with a $^1F_3$ ground term and a magnetic moment of 3.6 B.M. is the first example of a complex compound in which magnetism is solely attributed to orbital angular momentum.

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