Inorganica Chimica Acta, 198–200 (1992) 795–803

Strong exchange coupling between the lanthanide ions and the phthalocyaninato ligand radical in bis(phthalocyaninato)lanthanide sandwich compounds

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Abstract

A series of lanthanide phthalocyanine sandwich compounds with the formula $[(Pc^{2-})Ln^{III}(Pc^{1-})]$ have been synthesized and characterized. To a first approximation, the lanthanide ions exist in their normal trivalent state, while one of the phthalocyanine ligands exists in the normal dianionic state and the other exists as a monoanionic phthalocyanine radical. It is obvious from the magnetic behavior of these compounds that there is a strong magnetic interaction between the lanthanide f electrons and the phthalocyanine radical electron. Both antiferro- and ferromagnetic ground states have been observed in this series of compounds which depends on the symmetry and occupancy of the magnetic orbitals on the lanthanide ion. In some cases both the antiferro- and ferromagnetic states of a single system are observed in the temperature range studied. In these cases, the energy separation between states has been evaluated from the magnetic data.

Introduction

A variety of tetraazamacrocycles, such as the phthalocyanines, porphyrins and their derivatives have been extensively studied in order to model the behavior of naturally occurring porphyrinic macrocycles [1]. These compounds play an important role in biological processes, such as transport and storage of oxygen, nitrogen fixation and photosynthesis. Due to the propensity of high coordination, in this case octacoordination of the lanthanide ions, these ions are able to accommodate two tetraazamacrocycles in a sandwich like structure around the lanthanide ion. Compounds in which two porphyrin disks are held together at a fixed distance by a large rare earth cation could serve as models for energy transfer in biological systems [2].

Lanthanide phthalocyanine sandwich compounds with the formula $Ln(Pc)_2$ have been known for over twenty-five years [3]. 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 may be considered to be 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 and co-workers [4]. Other lanthanide sandwich compounds have essentially the same structure [5] in which the two phthalocyaninato rings are rotated approximately 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 UV, Vis and near-IR spectra and by elemental analysis.

Experimental

Synthesis

The lanthanide phthalocyanines were prepared by a method similar to those which are described in the literature [6–8]. Excess 1,2-dicyanobenzene (recrystallized from methanol) was mixed in an approximately 14:1 molar ratio with the appropriate lanthanide acetate and vigorously ground together by using a mortar and pestle. The mixture was then placed in a large reaction tube equipped with a water cooled condenser, heated in a sand bath at 280–300 °C for 4–5 h and cooled slowly. Unreacted dicyanobenzene collected on the sides of the reaction tube and condenser. The dark green product which formed was separated from the unreacted dicyanobenzene and reground. The product was then returned to a clean, dry reaction tube and heated in a sand bath at 300 °C under vacuum for 12–24 h. This process was repeated several times. The product was

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0020-1693/92/$5.00

washed with acetic anhydride and cold acetone, dissolved in a minimum amount of chloroform and gravity filtered to remove any free phthalocyanine which may have formed. This solution was separated on a 15×2 inch basic alumina column using a 5% methanol/toluene solution. In most cases, a green fraction eluted first, followed by a blue fraction. Some blue product remained on the top of the column and could not be eluted. Occasionally, a small amount of brown product could be detected which was previously determined [5] to be the linear polymer of 1,2-dicyanobenzene. The ratio of blue and green products obtained depended on the lanthanide used, such that as one moves to the left of the periodic table, more blue product is formed. The solution containing the green product was taken to dryness on a rotary evaporator and then dried in a vacuum oven. Although there has been much debate concerning the composition of these compounds [8–13], it has been determined that the green compound is of the composition most readily depicted, to a first approximation, as $(Pc^{2-})Ln^{3+}(Pc^{1-})$, where Ln equals Pr, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu; (Pc^{2-}) is the dianionic form of the phthalocyaninato ligand; and (Pc^{1-}) is the monoanionic radical form of the phthalocyaninato ligand. It has been discussed in the literature that there are two blue compounds that also evolve from this synthesis [7], namely, $(Pc^{2-})Ln^{3+}(Pc^{2-})H$ and $(Pc^{2})Ln^{3+}(Ac^{1-})$ where (Ac^{1-}) is the monoanionic acetato ligand. It has been shown that the blue compound that elutes is the $(Pc^{2-})Ln^{3+}(Pc^{2-})H$ compound [13] and it is assumed that the blue compound that remains on top of the column is the $(Pc^{2-})Ln^{3+}(Ac^{1-})$ compound. However, these compounds were not studied in this research. As discussed in the literature [2], the temperature at which the initial reaction occurs has a large effect on the products formed. It was seen that if the reaction temperature deviated by 20° or more above 300 °C, very little green product was obtained and the major product formed was a blue material which could not be eluted from the column and was assumed to be the $(Pc^{2-})Ln^{3+}(Ac^{1-})$ blue form.

Physical measurements

Low temperature magnetic susceptibility data were collected in the temperature range of 4.2–100 K using a Princeton Applied Research model 155 vibrating sample magnetometer (VSM) equipped with Janis Research Company model 153 liquid helium cryostat. Magnetic fields between 0 and 15 kOe were generated using a Magnion model H-96 electromagnet and a Magnion model HSR-1365 power supply. The magnetic field was regulated using a Magnion model FFC-4 field control unit and a Rawson-Lush model 920 MCM rotating coil gaussmeter. The magnetic field was periodically calibrated against lithium and proton NMR resonances using a Walker/Magnion model G-502 NMR gaussmeter. The sample temperature was monitored by using either a gallium-arsenide or gallium–aluminum-arsenide diode, which were purchased and calibrated by Lake Shore Cryotronics. The magnetometer signal output was calibrated using the standard, mercury tetrathiocyanatocobaltate(II), $HgCo(NCS)_4$ [14–16]. Powdered samples were packed into precision milled Lucite sample holders. Diamagnetic corrections of constituent atoms were made using Pascal's constants [17, 18].

High temperature magnetic susceptibility data in the range of 77–300 K were collected using a Faraday balance. The Faraday system is comprised of a Cahn 2000 electrobalance, an ANAC series 3472 100 mm electromagnet, an ANAC model 3610-I magnet control system and a Sorenson SRL 40-50 power supply. A magnetic field of ≈7500 G was used for all measurements with a field gradient of $\approx \pm 160$ G/cm generated by Georges Associates model 502 Lewis coils and the associated Georges Associates model 202 power supply. A liquid nitrogen dewar of local design was placed around the sample tube containing the He static exchange gas. The sample was allowed to warm slowly to room temperature and data were collected automatically. The sample temperature was monitored using a calibrated Lake Shore Cryotronics DT-500 silicon diode located approximately 7 mm below the sample. The magnetometer signal output was calibrated using $HgCo(NCS)_4$. The samples were contained in polycarbonate capsules obtained from Universal Plastics and Engineering Company and suspended from the electrobalance using a chain made of fine quartz tubing and fine gold chain. Diamagnetic corrections of constituent atoms were made using Pascal's constants.

Electron paramagnetic resonance (EPR) spectra were obtained using a Varian E-109 spectrometer system operated at X-band. The frequencies were monitored using a Hewlett-Packard model 5340 A frequency counter. Low temperature EPR spectra were obtained using an Oxford model ESR-910 continuous flow cryostat equipped with an AuFe/chromel thermocouple. The field was calibrated using the standard, diphenylpicrylhydrazyl (DPPH). Samples were contained in capillary tubes placed inside quartz sample tubes.

The data were fit to theoretical models using a Simplex [19–21] non-linear least-squares fitting routine. The function minimized was the sum of the squares of the residuals

$$R=\Sigma[(Q_i^{obs}-Q_i^{calc})^2/(Q_i^{obs})^2] \quad (1)$$

where Q_i is the physical quantity being fit.

Results and discussion

Spectroscopic and structural properties

The electronic spectra of the lanthanide bis(phthalocyanine) compounds have been thoroughly studied [6–8, 13, 22]. The results of these investigations have been used in this research to verify the composition of the products. The electronic spectra of these compounds reflect the individual transitions expected for the dianionic and monoanionic radical forms of phthalocyanine as well as an intervalence charge transfer band which accounts for the interaction between phthalocyanine species. The values of the UV, Vis and near-IR transitions for the lanthanide bis(phthalocyanine) compounds are given in Table 1.

By comparison of the powder patterns of the α, β and γ phases for $NdPc_2$ given by Darovskikh [23], the powder patterns of the compounds studied in this research very closely resemble those of the γ phase. From the structures given, it is assumed in this work that the lanthanide bis(phthalocyanine) sandwich compounds form a slightly distorted square antiprism with an angle of rotation of ≈ 41–$42°$. The metal to N_4 plane distances are not equivalent between the lanthanide ion and the two phthalocyanine rings. The average values of these distances range from ≈ 1.34 Å for $LuPc_2$ to ≈ 1.50 Å for $PrPc_2$. Both phthalocyanine rings are curved away from the lanthanide ion, however, it is likely that one phthalocyanine ligand is more distorted than the other [24] due to the inequality of the two ligands.

Magnetic properties

Three possibilities exist for the type of interaction between the lanthanide f electrons and the ligand based radical electron. The most obvious choice is that no interaction exists between the two and each behaves independently in terms of contribution to the magnetic susceptibility of the complex. It is also possible that these two species can interact either antiferromagnetically or ferromagnetically. In the case where no interaction exists, the magnetic susceptibility of the complex would be represented by

$$\chi_m = \frac{N\beta^2}{3kT}\left[g_L{}^2J(J+1) + g_e{}^2S(S+1)\right] \quad (2)$$

and the magnetic moment would be calculated using the equation

$$\mu_{eff} = \left[g_L{}^2J(J+1) + g_e{}^2S(S+1)\right]^{1/2} \quad (3)$$

where g_e is the free-electron g value equal to 2.0023.

TABLE 1. UV, Vis and near-IR transitions (in nm) for the lanthanide bis(phthalocyanine) sandwich compounds

$LnPc_2$	Soret[a]	$e_g \rightarrow a_{1u}$[b]	Q-band[a]	$e_g \rightarrow a_{1u}$[b]	CTI[c]
$LuPc_2$	320	458	658	917	1370
$YbPc_2$	322	458	660	917	1386
$TmPc_2$	320	460	660	915	1390
$ErPc_2$	322	460	662	913	1397
$HoPc_2$	322	460	664	913	1406
$DyPc_2$	322	460	666	914	1416
$TbPc_2$	322	460	666	909	1419
$GdPc_2$	322	458	670	912	1424
$PrPc_2$	<300	464	678	898	1770

[a] Soret and Q-bands from dianionic form of phthalocyanine. [b] Transitions due to a 'hole' in HOMO of monoanionic phthalocyanine. [c] Intervalence charge transfer bands $Pc^{2-} \rightarrow Pc^{1-}$.

The values of μ_{eff} for all of the trivalent lanthanides discussed have been calculated using the free ion term and the free ion plus radical term as discussed above. These values were compared to the limiting values found experimentally and are given in Table 2. Since, the majority of the complexes studied show an approximately 1 BM reduction from that of the free ion value, it is obvious that the lanthanide f electrons and the ligand based radical electron do indeed interact. Based on the magnitude of the moment reduction, as discussed below, this interaction is very strong.

A model of the energy level splitting for the lanthanide ion including a strong interaction with the phthalocyanine radical is shown in Fig. 1, with Yb^{3+} as the example. The relative order of perturbations to the free ion are now given by

$$e^2/r_{ij} \geqslant \lambda \mathrm{L}\cdot\mathrm{S} \gg J < V_{cf} \approx kT$$

where J represents the coupling between the lanthanide free ion ground state term and the phthalocyanine radical electron. Due to the strength of this interaction, it is possible to calculate a new term symbol for all of the complexes based on a linear combination of the ${}^{2S+1}L_J$ term of the lanthanide and the ${}^2S_{1/2}$ term of the ligand radical. For an antiferromagnetic interaction, this new term would be ${}^{2S}L_{J-1/2}$, for gadolinium through lutetium where $J=L+S$. Similarly for the ferromagnetically coupled state this new term would be designated ${}^{2S+2}L_{J+1/2}$, where S and J are the free ion values for the ground state of the lanthanide ion in question. In the case of praseodymium, where $J=L-S$, the new terms would be designated as ${}^{2S}L_{J+1/2}$ and ${}^{2S+2}L_{J-1/2}$, for the antiferromagnetic and ferromagnetically coupled states, respectively. As illustrated in Fig. 1, depending on the magnitude of the antiferromagnetic–ferromagnetic splitting, ΔE, it is possible for the ferromagnetically coupled state to become populated at high temperatures.

From the Van Vleck equation given previously, the magnetic susceptibility for these complexes including both antiferromagnetic and ferromagnetic states can be given by eqn. (4)

TABLE 2. Theoretical values of μ_{eff} (in BM) for all the trivalent lanthanides using the free ion term and the free ion plus radical term, as discussed in the text, as compared to the limiting values found experimentally for the lanthanide bis(phthalocyanine) sandwich compounds

$LnPc_2$	Lanthanide free ion	Lanthanide–radical interaction			Limiting value experimental
		None	Ferromagnetic	Antiferromagnetic	
$PrPc_2$	3.58	3.97	2.65	4.52	2.5
$GdPc_2$	7.94	8.12	8.94	6.93	6.9
$TbPc_2$	9.72	9.87	10.75	8.70	8.6
$DyPc_2$	10.63	10.76	11.67	9.62	10.2
$HoPc_2$	10.60	10.75	11.59	9.58	9.5
$ErPc_2$	9.57	9.74	10.61	8.55	8.2
$TmPc_2$	7.63	7.78	8.59	6.52	7.2
$YbPc_2$	4.52	4.84	5.59	3.46	4.3
$LuPc_2$	0	1.73			1.7

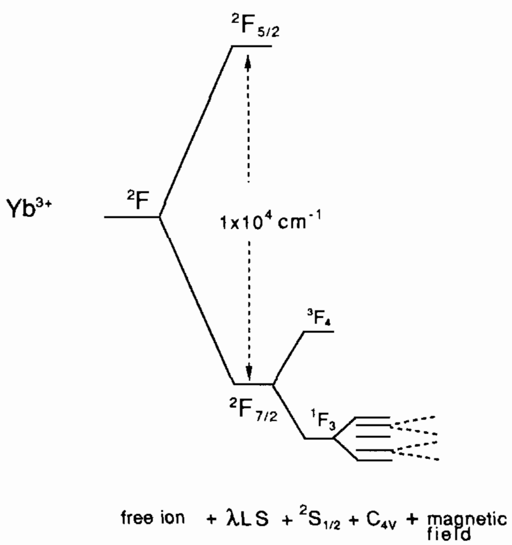

Fig. 1. A model of the energy level splitting for the lanthanide ions, including a strong interaction with the phthalocyanine ligand radical, with Yb^{3+} given as the example.

$$\chi=\frac{N\beta^2}{kT}\left\{\frac{\sum_j(m_{j0}g_{j0})^2+\sum_j(m_{j1}g_{j1})^2\exp\left(\frac{-\Delta E}{kT}\right)}{(2J_0+1)+(2J_1+1)\exp\left(\frac{-\Delta E}{kT}\right)}\right\} \tag{4}$$

For simplicity, it is assumed that all multiplet states are equally populated, since the crystal field splitting is assumed to be small in this case. The new ground state energy is set equal to zero and the new excited state energy is set equal to ΔE, so the relative energy separation between the two states can be determined. The first order Zeeman terms $E_n{}^1$ are equal to $m_j g_j \mu_\beta$ and second order Zeeman terms are neglected. The following is a detailed description of the magnetic behavior for each of the lanthanide bis(phthalocyanine) compounds studied. The experimental magnetic susceptibility data, given in units of μ_{eff} versus temperature, for all of the lanthanide bis(phthalocyanine) compounds studied are given in Fig. 2.

Praseodymium

From the experimental data, taken from 4.2–300 K, it can be seen that the limiting moment at 300 K is equal to ≈2.5 BM. The data were therefore fit to the Curie–Weiss model as follows

$$\chi_m=\frac{Ng_L{}^2\beta^2}{3k(T-\theta)}[J(J+1)] \tag{5}$$

where J was input as a constant and the data was fit using a non-linear Simplex least-squares fitting routine, as described earlier, to g and θ. Here θ is the Weiss constant which corrects for the less than ideal circumstances imposed by the Curie law alone. With J equal

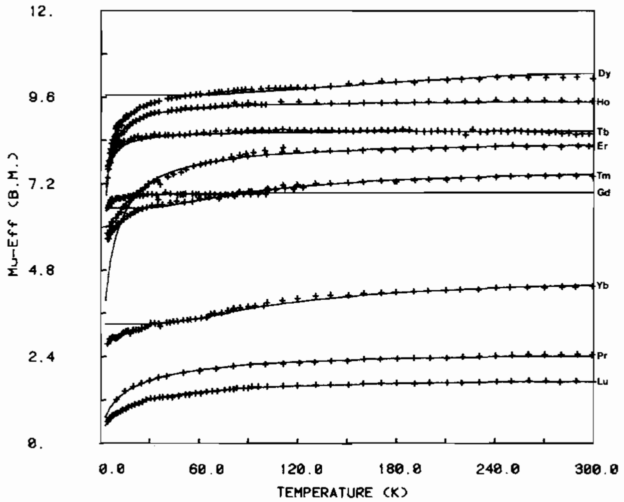

Fig. 2. The experimental magnetic susceptibility data, given in units of μ_{eff} vs. temperature, for all of the lanthanide bis(phthalocyanine) sandwich compounds studied.

to 7/2 the data was fit with the parameters $g=0.65$ and $\theta=34.64$ K with an R value for the fit of 0.0244.

The fit to the data was approached from several different directions. Attempts to fit the data using a J value other that 7/2 did not give reasonable fits. When J was set as 7/2, all fits converged with the same set of parameters as those given above, regardless of the initial parameters input. Therefore, it may be concluded that the parameters for the best fit to the data are given above and are not simply the result of a local minimum. Praseodymium is unique in that it is the only example in the series of compounds studied in this work where the ground state is that which results from the ferromagnetic coupling of the lanthanide and ligand electrons. An explanation of this interaction will be discussed in the following section.

Gadolinium

From the experimental data taken from 4.2–100 K, it can be seen that the moment levels off at $T<10$ K with a value of 6.9 BM which remains constant up to 100 K. Since it is well known that compounds of trivalent gadolinium almost always obey the Curie law and provide, by far, the best examples of the free ion model, several attempts were made to fit this data to the Curie–Weiss equation given previously.

All attempts to fit the data to the Curie–Weiss law with $J=7/2$ and $g=2.00$ were fruitless. With $J=3$, and g fixed at 2.00, a value of $\theta=-0.47$ K was obtained with an R value for the fit of 0.0122. When all parameters were allowed to vary, the parameters obtained were $g=2.01$ and $\theta=-0.51$ K with an R value of 0.0118. Both fits show excellent agreement to the data and appear to be equivalent within the limits of error. Therefore, it can be concluded that the ground state for $GdPc_2$ is a $^7S_3$ state which arises from the strong antiferromagnetic coupling between the gadolinium f electrons and the phthalocyanine radical electron. The ferromagnetically coupled $^9S_4$ excited state does not contribute to the magnetism of this compound in the temperature range studied.

Terbium

From the experimental data taken from 4.2–300 K, it can be seen that the magnetic moment levels off near 8.6 BM. Initially, only the data from 0–100 K obtained from the vibrating sample magnetometer were used in the SIMPLEX fitting routine. From this set of data, with $J=11/2$, the best fit values obtained using the Curie–Weiss equation were found to be $g=1.46$ and $\theta=-1.54$ K with an R value of 0.0201. When the experimental data from 77–300 K obtained from the Faraday balance were combined with this data, the new best fit parameters were found to be $g=1.45$ and $\theta=-1.45$ K with an R value of 0.0230. Both show excellent agreement with the experimental data and appear to be equal within experimental error.

All attempts to fit the data with J values other than 11/2 were unsuccessful. The values for g and θ were allowed to vary freely during the SIMPLEX fitting routine, and these parameters always converged to the same values as those given above. Therefore, for the case of $TbPc_2$, it is obvious that the ground state of the complex is $^6F_{11/2}$, a state which arises from strong antiferromagnetic coupling between the terbium f electrons and the phthalocyanine radical electron. The $^8F_{13/2}$ excited state, which arises from the ferromagnetic coupling as described previously, does not appear to contribute to the magnetism in the temperature range studied.

Dysprosium

The experimental data taken from 4.2–300 K do not follow simple Curie–Weiss behavior. At very low temperatures (4.2–60 K), the data can be fit to the Curie–Weiss law with $J=7$, $g=1.30$ and $\theta=-2.68$ K. However, above this temperature, deviations are evident. Due to the inability to fit the data for $J=7$, many attempts were made to fit the data to the $^6H_{15/2}$ state, with and without the presence of the ligand radical electron. All attempts were unsuccessful, ruling out all other possibilities considered. Thus the data were fit to a model which includes both the antiferromagnetic coupled ground state and the ferromagnetically coupled excited state as given by eqn. (4) and depicted in Fig. 1.

This model does not fit the data at very low temperatures, since the model assumes for simplicity that all m_j states are equally populated. This of course is not accurate at low temperatures and depends on the magnitude of the crystal field which exists as a small perturbation for both the antiferro- and ferromagnetically coupled states. At temperatures above approximately 40 K the data can be fit to this model with $J_0=7, J_1=8, g_0$ and g_1 fixed at 1.29 and 1.375, respectively, and ΔE equal to 216 cm^{-1}. This fit gave an R value of 0.00227 with $T_{\min}$ set at 40 K. Dysprosium bis(phthalocyanine) is the first compound in the series discussed that shows the presence of the ferromagnetically coupled excited state and lends further credence to the model of the magnetic behavior proposed.

Holmium

From the experimental data taken from 4.2–300 K, it can be seen that the magnetic moment levels off near 9.5 BM. The best fit values obtained using the Curie–Weiss equation given above with $J=15/2$ were found to be $g=1.19$ and $\theta=-2.72$ K with an R value of 0.0210. This fit shows excellent agreement with the experimental data. All attempts to fit the data to the Curie–Weiss equation with $J=7$, both with and without the presence of a non-interacting radical electron, were unsuccessful. The values for g and θ were allowed to vary freely during the SIMPLEX fitting routing, and always converged to the same values as those given above. Therefore, in the case of $HoPc_2$, it is obvious that the ground state for this system is the $^6F_{11/2}$ state which arises from the strong antiferromagnetic coupling between the holmium f electrons and the phthalocyanine radical electron. The $^8F_{13/2}$ excited state which arises from the ferromagnetic coupling as described previously, does not appear to contribute to the magnetism in the temperature range studied.

Erbium

From the experimental data taken from 4.2–300 K, it can be seen that the magnetic moment levels off near 8.2 BM. Due to the significant decrease in the experimental magnetic moment from that which is expected for the $^4I_{15/2}$ ground state, the data were fit to the Curie–Weiss equation assuming an antiferromagnetic interaction between erbium and phthalocyanine electrons. Above 15 K the data were fit to the model described with a g value of 1.124 and a θ value equal to -10.66 K. This fit gave an R value of 0.00983. This data could not be fit to any of the other models described above. At temperatures below 15 K the data could not be fit. The inability to fit the data below 15 K and the slightly low g value from that which is expected indicate that the effects of the crystal field are not well understood in this case. Further calculations are necessary.

Thulium

The experimental data taken from 4.2–300 K do not follow simple Curie–Weiss behavior. At very low temperatures (up to 60 K), the data appears to level off near 6.5 BM. However, above this temperature, deviations are evident. Due to the inability to fit the data to the Curie–Weiss law with $J=11/2$, many attempts were made to fit the data to the $^3H_6$ state, with and without the presence of the ligand radical electron. All attempts were unsuccessful, ruling out all other possibilities considered. Thus the data were fit to a model which includes both the antiferromagnetic coupled ground state and the ferromagnetically coupled excited state.

As expected, this model does not fit the data at low temperatures, since the model assumes for simplicity that all m_j states are equally populated. This of course is not accurate at low temperatures and depends on the magnitude of the crystal field which exists as a small perturbation for both the antiferro- and ferromagnetically coupled states. At temperatures above approximately 30 K, the data can be fit to this model with $J_0=11/2$, $J_1=13/2$, g_0 and g_1 equal to 1.09 and 1.23, respectively, and ΔE equal to 98 cm^{-1}. This fit gave an R value of 0.01292 with T_{min} set at 15 K. Thulium bis(phthalocyanine) is another example in the series of lanthanide bis(phthalocyanine) sandwich compounds that shows the presence of the ferromagnetically coupled excited state and strengthens the validity of the model of the magnetic behavior proposed.

Ytterbium

The experimental data taken from 4.2–300 K do not follow simple Curie–Weiss behavior. At very low temperatures (up to 60 K), the data begin to level off near 3.4 BM. The low temperature data were fit to the Curie–Weiss model giving the values $g=1.04$, $\theta=-4.66$ K, with an R value for the fit of 0.0186. This model was fit using $J=3$ and appears to closely resemble the model for strong antiferromagnetic coupling. Above this temperature, deviations are evident.

Due to the inability to fit all of the data to the Curie–Weiss law with $J=3$, an attempt was made to fit the data to the $^2F_{7/2}$ state, with and without the presence of the ligand radical electron. No reasonable fit could be obtained. Thus the data were fit to a model which includes both the antiferromagnetic coupled ground state and the ferromagnetically coupled excited state.

As expected, this model does not fit the data at very low temperatures, since the model assumes for simplicity that all m_j states are equally populated. This of course is not accurate at low temperatures and depends on the magnitude of the crystal field which exists as a small perturbation for both the antiferro- and ferromagnetically coupled states. At temperatures above approximately 30 K the data can be fit to this model with $J_0=3$, $J_1=4$, g_0 and g_1 equal to 0.95 and 1.25, respectively, and ΔE equal to 125 cm^{-1}. This fit gave an R value of 0.0401 with T_{min} set at 15 K.

Due to the relatively large magnetic dilution in ytterbium bis(phthalocyanine), especially as compared to others in this series, the data are somewhat noisy. Therefore, the accuracy of the fit may be decreased. Several sets of data were taken and fit in an attempt to improve the validity of the fit and all sets of data, although noisy, led to nearly the same fit values.

Ytterbium bis(phthalocyanine) is another example in this series of compounds which exhibits the presence of both the antiferro- and ferromagnetically coupled states of the lanthanide and phthalocyanine radical electrons. All evidence leads to the conclusion that the model derived here is appropriate in this series of compounds. The data could not be fit to the $^2F_{7/2}$ free ion state, and no mixing in of the $^2F_{5/2}$ at 10 000 cm^{-1} can possibly exist and can thus be ignored. The possibility that the ytterbium might exist in a state other than its trivalent state was also explored, but none were able to adequately account for the magnetic behavior. It is important to note that the new ground state in this system, a $^1F_3$ state, with a magnetic moment in the order of 3.6 BM, containing no formally unpaired electrons. This is the first known example of a complex compound in which magnetism of such a large magnitude can be attributed solely to orbital angular momentum.

Lutetium

The experimental data for lutetium bis(phthalocyanine) exhibit a limiting moment near 1.75 BM. The best fit values to the Curie–Weiss law gives a g value equal to 2.12 with $\theta = -38.60$ K and an R factor for the fit of 0.05826. Again, the data are noisy due to magnetic dilution (1 spin/1200 a.m.u.), but the fit remains valid. The relatively large g and θ values are attributed to intercluster interactions between unpaired electrons on adjacent lutetium bis(phthalocyanine) species. This is further validated by the EPR spectra seen for lutetium bis(phthalocyanine) as discussed later in this text.

Electron paramagnetic resonance

When the effects of orbital moment are small, resonances are manifested as small deviations (from g_e) in the g value. This is the case for the free electron which exists in the lutetium bis(phthalocyanine) system which exhibits a g value of 2.01 at 298 K and a g value of 2.00 at 7.2 K as seen in Fig. 3. The fact that the linewidth increases as the temperature is lowered is attributed to the intercluster interactions which exist between unpaired electrons on adjacent lutetium bis(phthalocyanine) species. Since spin–spin interactions result from the small magnetic fields that exist on neighboring paramagnetic ions, the total field at the ion is slightly altered and the transition energies appear to be shifted. A distribution of energy results which produces a broadened spectrum. The EPR spectra of lutetium bis(phthalocyanine) show a linewidth of 1.5 Oe at 298 K and 11 Oe at 7.2 K.

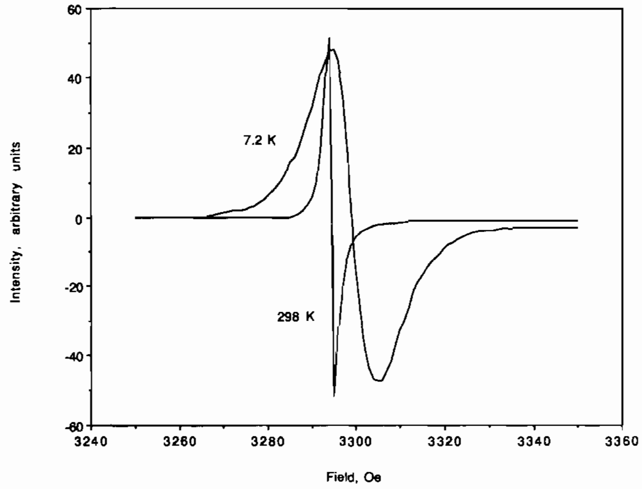

Fig. 3. The EPR spectra of lutetium bis(phthalocyanine) at 298 and 7.2 K.

Since the phthalocyanine radical electron which exists in the lanthanide bis(phthalocyanine) compounds (other than lutetium) show very strong coupling with the lanthanide f electrons, EPR transitions at or near the free electron g value are not expected. Since the new states formed by this coupling contain large uncompensated orbital angular momentum, the deviations from g_e are expected to be very significant. As discussed earlier, strong spin–orbit coupling interactions exist in most lanthanide compounds and, therefore, J remains a good quantum number. After this, the ligand field splitting is treated as a perturbation to the J states. EPR transitions in these systems occur between crystal field states or between states such as Kramer's doublets, which are split only in a magnetic field.

The EPR spectra of the lanthanide bis(phthalocyanine) compounds where the lanthanide is praseodymium, gadolinium, dysprosium, holmium, erbium, thulium or ytterbium show very complicated EPR spectra with no transitions at or near $g = 2$, except for the spectrum of praseodymium bis(phthalocyanine) in which the transition at $g = 2$ may simply be fortuitous. However, the very complicated task of calculating the crystal field effects in these systems is necessary in order to adequately interpret the EPR spectra in these systems. This work is currently underway.

Pathways for exchange

Two possible mechanisms exist to explain the phenomenon of spin–spin coupling interactions. The first possibility is direct contact between adjacent magnetic orbitals. The second possibility is superexchange, where the magnetic orbitals overlap with filled orbitals and are delocalized in this manner. The rules which govern the exchange depend on the occupancy and symmetry of the orbitals involved [25].

If there is finite overlap of the magnetic orbitals on adjacent species, then according to the Pauli principle, the spins must be aligned antiparallel. The spins are paired and the exchange is antiferromagnetic. Anderson [26] has labelled this as kinetic exchange. When the magnetic orbitals are orthogonal, their spins are aligned parallel and the exchange is ferromagnetic. Anderson has labelled this as potential exchange. A magnetic orbital on one ion may also overlap with an empty orbital on a second magnetic ion. Intra-atomic coupling of the electrons in these orthogonal magnetic orbitals is also ferromagnetic. Calculations indicate that $J_{ij}(\text{kinetic}) \gg J_{ij}(\text{potential})$, and therefore when both kinetic and potential exchange are possible the kinetic contribution is usually the largest.

If there is little direct overlap of magnetic orbitals, finite exchange across filled d orbitals plays an intermediary role in the exchange between magnetic ions.

Finite overlap of both magnetic orbitals with the intermediate filled d orbitals would lead to antiferromagnetic exchange coupling as described above. Overlap of one magnetic ion with the filled d orbitals, which in turn is adjacent to an orthogonal orbital on the other magnetic ion or overlaps with an empty orbital on that ion, would lead to a ferromagnetic contribution to the exchange.

The π molecular orbitals of metal-free phthalocyanine were obtained by Chen [27] using Hückel-type molecular orbital calculations. Although the symmetry of the phthalocyanine in Chen's study was assumed to be D_{2h}, it is easily converted into C_{4v} symmetry as necessary for this study. The symmetry of the HOMO of phthalocyanine which contains the unpaired electron is a_u. It is assumed that the iso-indoline (inner) nitrogens play the key role in bonding and electron exchange in these lanthanide bis(phthalocyanine) compounds. The linear combination of atomic orbitals (LCAOs) for the iso-indoline nitrogens is

$$\Psi = N_a - N_b + N_c - N_d$$

where a–d consecutively label the four inner nitrogens on the phthalocyanine. When the LCAOs of the two phthalocyanines are combined in the symmetry appropriate for the lanthanide bis(phthalocyanine) compounds, two new molecular orbitals arise. These two orbitals transform as b_1 and b_2 in C_{4v} symmetry as described below.

The two phthalocyanines are designated as 'Ring A' and 'Ring B'. These two rings can be combined in two configurations, 'A + B' and 'A − B' as depicted in Fig. 4, and the two new molecular orbitals formed from this combination transform as b_1 and b_2 in C_{4v} symmetry.

Based on the geometry of the f orbitals as depicted by Becker [28] the splitting of the f orbitals in C_{4v} symmetry can be determined. It can be seen that f_{xyz} lies highest in energy since 4 of 8 lobes point directly toward the 4 inner nitrogens on one of the phthalocyanine ligands. The $f_{z(x^2-y^2)}$ orbital, although very close in energy to the f_{xyz} orbital, is slightly lower in energy since the second phthalocyanine is rotated only 42° and therefore 4 of 8 lobes are not directly pointed toward the phthalocyanine nitrogens. Both the $f_{x(z^2-y^2)}$ and $f_{y(z^2-x^2)}$ have two of 8 lobes which are directed toward the phthalocyanine nitrogens. Therefore, they are of lower energy than the $f_{z(x^2-y^2)}$ orbital, but still higher in energy than the f_{z^3}, f_{x^3} and f_{y^3} set in which no lobes are pointed at or near the phthalocyanine nitrogens. The (f_{z^3}, f_{x^3}, f_{y^3}) set are slightly split in energy since the two phthalocyanines are not centrosymmetric and therefore the f_{z^3} orbital is slightly higher in energy than the f_{x^3} and f_{y^3} orbitals.

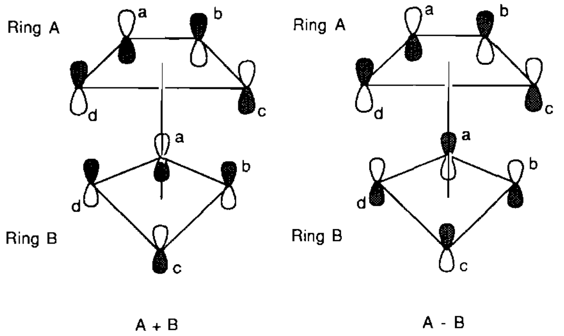

Fig. 4. Schematic diagram of the LCAOs formed from the iso-indoline nitrogens for the two phthalocyanine ligands in the lanthanide bis(phthalocyanine) sandwich compounds.

Based on the arguments given above, the splitting of d orbitals in C_{4v} symmetry is also easily determined. However, since all of the 4d orbitals of the lanthanides are filled, the exact energy of each of the orbitals is not as significant as the symmetry which they possess.

Conclusions

Since the unpaired electron from the phthalocyanine ligands lies in the molecular orbital with B_2 symmetry, interaction with the B_2 orbital of the f orbital set would lead to magnetic exchange. Since the f_{xyz} orbital of the f set possesses B_2 symmetry and is highest in energy, it is a magnetic orbital (one unpaired electron) as long as the f electron shell is more than half-filled. This is the case for the lanthanides gadolinium through ytterbium and therefore leads to antiferromagnetic exchange in these systems. In the case of praseodymium, the less than half-filled f electron shell leaves the B_2 orbital empty and therefore leads to a ferromagnetic coupling with the phthalocyanine radical electron.

Likewise, if the d orbitals are involved, overlap is possible between the B_2 orbital of the phthalocyanine radical and the filled B_2 orbital (d_{xy}) of the 4d set which in turn overlaps with the B_2 orbital of the f orbital set. If the B_2 orbital of the f orbital set contains one unpaired electron then the exchange is antiferromagnetic, as is the case for gadolinium though ytterbium. If the B_2 orbital of the f orbital set is empty then the exchange is ferromagnetic, as is the case for praseodymium. Thus, the pathways for exchange based on orbital symmetry and occupancy are able to describe the magnetic behavior of the lanthanide bis(phthalocyanine) compounds as seen previously.

Acknowledgements

This work was funded by the Office of Naval Research, the Department of Education and the National Science Foundation.

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