J. Phys. Chem. A **2001,** *105,* 7525−7533

Distinction between Light and Heavy Lanthanide(III) Ions Based on the ^{1}H NMR Spectra of Heteroleptic Triple-Decker Phthalocyaninato Sandwich Complexes

Dennis P. Arnold* and Jianzhuang Jiang†

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology,
G.P.O. Box 2434, Brisbane 4000, Australia

Received: February 14, 2001; In Final Form: May 30, 2001

The ^{1}H NMR spectra of two series of heteroleptic triple-decker phthalocyaninato sandwich complexes of the rare earth(III) ions have been recorded. The ligands comprise unsubstituted phthalocyanine (Pc) and 2,3,9,10,16,17,23,24-octakis(1′-octyloxy)phthalocyanine (Pc*), and the complexes are of the form PcMPc*MPc (series 1) and PcMPc*MPc* (series 2), where M = Pr − Tm (except Pm, Gd). In some cases, the homoleptic complexes Pc*MPc*MPc* (series 3) were also available. The chemical shifts of five proton positions in series 1, and 10 positions in series 2 were compared with the shifts for the analogous complexes of the diamagnetic yttrium(III) ion. The experimental lanthanide-induced shifts (LIS) were separated into the contact and dipolar contributions using the crystal-field dependent methods of Reilley and co-workers. This work represents the first analysis of LIS in triple-decker phthalocyaninato lanthanide complexes. The results showed a dominance of dipolar contributions but also revealed that contact influences cannot be ignored, even for protons located in the peripheral alkoxy substituents. Analysis by graphical and matrix methods indicates that there is a clear discontinuity in the data between terbium and dysprosium, whereby the metals Nd, Sm, Eu and Tb possess a positive hyperfine coupling term F_i, and the later metals Dy, Ho (limited data), Er and Tm require a negative contact term. This change is coincident with a near-halving of the dipolar term $G_i{\cdot}A_2^0\langle r^2\rangle$ for the later metals. The properties of praseodymium are anomalous, in that its complexes are readily demetalated, and its NMR behavior places it in the second group of metal ions, despite its early position in the lanthanide series. Use of crystal-field independent analysis shows that the discontinuity near the middle of the series is related to variation in both the hyperfine electron−nuclear coupling constant and the crystal-field properties of the metal ions, rather than to gross changes in geometry.

1. Introduction

The related aromatic macrocyclic pigments, porphyrins and phthalocyanines (Pc), have fascinated chemists for many years. The porphyrins were originally of interest because of their significance in biology, and the phthalocyanines by virtue of their use as dyestuffs. More recently, a plethora of investigations across a broad range of disciplines has resulted in a voluminous literature on all aspects of these compounds, including their proposed uses in medicine, nanotechnology, and molecular electronic devices of various kinds.[1] These pigments can form complexes with almost the complete Periodic Table of elements, and the sandwich complexes with rare earth, actinide, early transition and main group metal ions represent a particularly interesting group.[2] With such metal ions in the 3+ oxidation state (i.e., mainly, the rare earths), neutral double-decker complexes with the stoichiometry ML_2 formally comprise one L^{2-} and one $L^{\cdot-}$ macrocycle, i.e., there is a more-or-less delocalized "hole" in the π-electron framework. There is also a second series of complexes that are triple-decker sandwiches, with the stoichiometry $M^{III}{}_2L_3$, in which the ligands are in the normal diamagnetic 2- state. Paramagnetism in these latter compounds stems only from the unpaired f electrons of the rare earth ion, and ^{1}H NMR spectra can be readily recorded for many such species. Indeed they can exhibit the usual spectacular "shift reagent" effects when appropriate metal ions are complexed in the sandwich. The inherent "organic" paramagnetism of the radical anion-containing double-deckers often precludes observation of their NMR spectra.

The literature on the NMR spectroscopy of these groups of compounds has been reviewed recently,[2c] so it will not be repeated here in detail. The few reports on phthalocyaninato complexes have been largely confined to complexes of diamagnetic lutetium(III), and for the ML_2 complexes, to the nonradical $[ML_2]^-$, HML_2, or $[ML_2]^+$ species,[3,4] usually examined in situ after addition of reducing or oxidizing agents. So far, reports on the NMR spectra of double-decker Pc complexes of paramagnetic rare earth ions are restricted to those of Konami on $[MPc_2]^-$ (M = Y, Pr−Lu, except Pm)[3] and of Jiang and Ng on Eu complexes (also as the anions) of alkyl- and alkoxy-substituted Pc.[4d] There has been only one report on the NMR spectra of homoleptic triple-decker Pc complexes, namely $La_2[Pc(OC_4H_9)_8]_3$ and $Lu_2[Pc(OC_4H_9)_8]_3$.[5] The 3+ ions of both these metals are diamagnetic. Jiang et al. reported the NMR spectra of heteroleptic Pc/tetraarylporphyrin triple-deckers of europium and samarium,[6] and we reported the spectra of triple-decker complexes of Eu with Pc and nickel(II) bis(octaethylporphyrinyl)butadiyne.[7]

The present work is concerned with heteroleptic phthalocyaninato triple-decker complexes containing unsubstituted parent Pc and the symmetrically octasubstituted ligand hence-

---

* To whom correspondence should be addressed. Fax: 61 7 3864 1804. E-mail: d.arnold@qut.edu.au.

† Permanent Address: Department of Chemistry, Shandong University, Jinan 250100, P. R. China. Fax: 86 531 856 5211. Email: jzjiang@sdu.edu.cn.

10.1021/jp0105847 CCC: $20.00

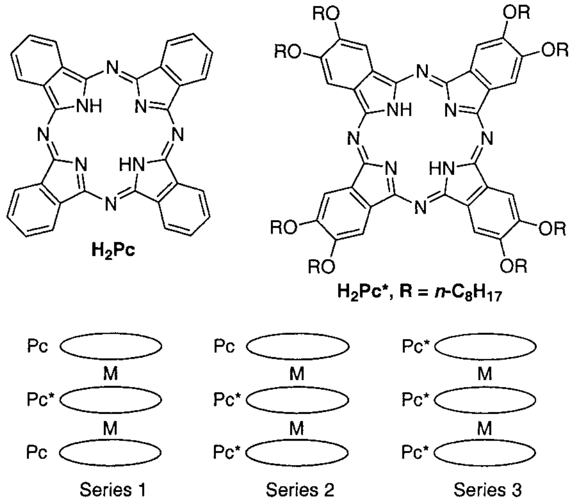

Figure 1. Structures of the ligands and the three series of triple-decker complexes.

forth denoted Pc* [= 2,3,9,10,16,17,23,24-octakis(1′-octyloxy)-phthalocyanine] (Figure 1). Our recent synthetic studies have produced, for the first time, two series of complexes, the symmetrical PcMPc*MPc (denoted "series 1", M = Y, Nd−Tm, except Pm, Gd) and the lower symmetry PcMPc*MPc* ("series 2", M = Y, Pr−Tm, except Pm, Gd). The syntheses and general characterization will be reported elsewhere.[8] The complex PcPrPc*PrPc* was not obtained pure, even after repeated chromatography, and was contaminated with both PcPrPc*PrPc and H_2Pc*. Moreover, it was subject to demetalation in solution. In the case of the earlier metals Pr, Nd, and Sm, the homoleptic complexes Pc*MPc*MPc* ("series 3") were also available in very small amounts.[8a] The corresponding homoleptic complex of Eu was available from other work.[8b]

By a combination of comparisons between/among the two/three series, and $^1H-^1H$ correlation spectroscopy, we have been able to assign almost all the signals in the spectra, with exceptions to be noted below. Although the *n*-octyloxy chains (included to improve solubility) made complete assignments difficult in some cases, the length of these chains enabled comparisons to be made of induced shifts at extended distances from the paramagnetic cores, as well as for the protons directly attached to the Pc and Pc* rings. Moreover, these studies would be virtually impossible with the unsubstituted Pc complexes, because of their insolubility in common solvents, a manifestation of their strong aggregation tendencies. In their study of $[MPc_2]^-$ (M = Y, Pr−Lu, except Pm), Konami et al.[3] analyzed their chemical shift data by methods used to interpret shifts induced by lanthanide shift reagents (LSR).[9−18] Buchler and co-workers discussed similar effects and conducted modeling studies concerning both ^1H and ^{13}C NMR spectra of the triple-decker octaethylporphyrinato (OEP) complexes of the lighter paramagnetic rare earth(III) ions Ce, Pr, Nd, Sm, and Eu.[19] Given the almost complete absence of literature on the NMR spectra of Pc-containing triple-deckers of paramagnetic lanthanides, we took this opportunity to examine our data in detail. We report here the paramagnetic shifts of our complexes and their treatment by both crystal-field dependent and independent methods. A discontinuity in behavior between the sets Nd−Tb and Dy−Tm was revealed, and this is shown to be electronic in nature, with effects on both the contact and dipolar parameters. In addition, the complex PcPrPc*PrPc* occupies the anomalous position of being an early member of the lanthanides, yet fitting better with the parameters derived for the late members.

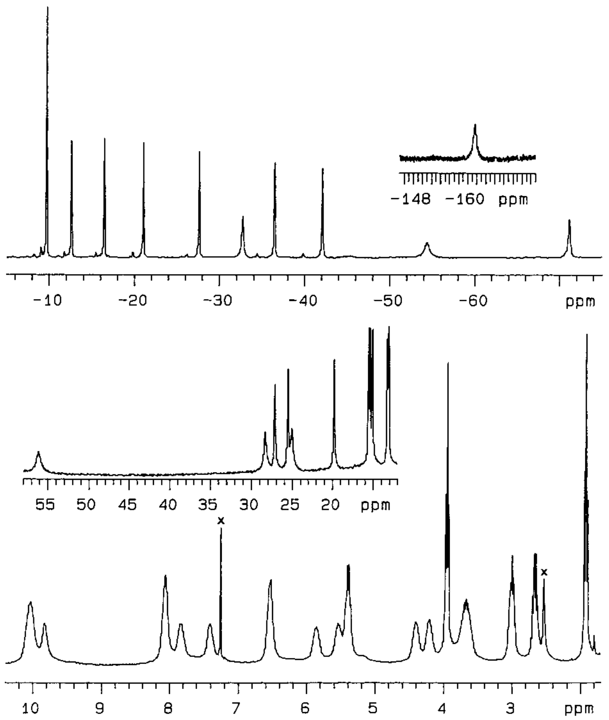

Figure 2. ^1H NMR spectra of PcTbPc*TbPc (upper two traces) and PcTmPc*TmPc* (lower two traces). The vertical and horizontal scales differ on each spectrum for clear display of all resonances; see Table 1 for assignments.

2. Results and Discussion

Assignment of the Spectra. The chemical shift data to be analyzed below are collected in Table 1. As examples of the results obtained, we show spectra for one series 1 complex (PcTbPc*TbPc, with upfield LIS) and one series 2 complex (PcTmPc*TmPc*, with downfield LIS) in Figure 2. The assignment of the spectra for the diamagnetic yttrium complexes was straightforward because of the resolved multiplicity in the signals for the alkyl chain protons, the narrow lines, and the availability of both PcYPc*YPc and PcYPc*YPc*. The presence of fine structure in the α and β signals for the unsubstituted Pc ring(s) allowed their differentiation from the Pc* α protons. COSY study allowed assignment of all the alkyl chain protons, although in some cases, the actual signals were overlapped and unresolved in the 1D spectrum. The diastereotopic OCH_2 protons on the outer Pc* ring in PcYPc*YPc* appeared as distinct signals at 4.24 and 4.64 ppm. In these series 2 complexes, the OCH_2 protons on the inner Pc* ring are also intrinsically nonequivalent, but for the yttrium complex, this results only in slight broadening of the signal. For the complexes of paramagnetic metal ions, this separation is distinct. Assignment of signals for the rest of the series followed the same logic of internal comparison of the series 1, 2, and where available, series 3 species, COSY studies, and integration. This made assignment of the Eu, Er and Tm complexes fairly straightforward because of their increasingly large downfield induced shifts. Similarly, the very large upfield shifts due to the presence of Tb and Dy assisted in the assignments. The Sm complexes exhibited, as expected, only very small upfield shifts, and the lines are correspondingly narrow, allowing observation of fine structure in the Pc α and β signals. Likewise, for the Nd complexes, with moderate upfield induced shifts, the Pc, Pc*, OCH_2, and CH_3 signals could be assigned. A problem arose with the Ho complexes because extreme broadening of the signals meant only those for protons in the alkyl chains were observed. These

TABLE 1: Selected ^{1}H NMR Data^a for Triple-deckers (CDCl$_3$, 19 ± 1 °C)

compound	ring	Pc* α	Pc α	Pc β	OCH$_2$^{b}	CH$_3$
PcYPc*YPc	in	8.29			5.04t	1.12t
	out		8.57dd	7.94dd		
PcYPc*YPc*	in	8.34			5.07m	1.09t
	out	8.00	8.59 dd	8.01dd	4.64m/i 4.24m/o	0.93t
PcPrPc*PrPc*	in	−4.04			−0.37br −0.6br^c	0.37t
	out	3.83	3.91	5.13	2.80dt/o 1.63m/i	0.67t
Pc*PrPc*PrPc*	in	−3.18			−0.26brt	0.37t
	out	3.92			2.83dt/o 1.66dt/i	0.65t
PcNdPc*NdPc	in	1.74			2.20brt	0.72t
	out		6.37	6.64		
PcNdPc*NdPc*	in	1.62			2.13m 2.01m	0.69t
	out	5.70	6.24	6.58	3.42dt/o 2.95dt/i	0.77t
Pc*NdPc*NdPc*	in	1.76			2.00brt	0.68t
	out	5.78			3.46dt/o 2.95dt/i	0.78t
PcSmPc*SmPc	in	6.63			4.30t	1.02t
	out		8.01dd	7.59dd		
PcSmPc*SmPc*	in	6.67			4.27m^c	1.01t
	out	7.40	8.00dd	7.61dd	4.27m/i^c 4.07dt/o	0.91t
Pc*SmPc*SmPc*	in	6.53			4.08^c	1.00t
	out	7.37			4.21/i 4.08/o^c	0.92t
PcEuPc*EuPc	in	12.28			6.61t	1.40t
	out		9.95m	8.60m		
PcEuPc*EuPc*	in	12.28			6.68dt 6.57dt	1.34t
	out	9.20	10.01	8.65	5.61dt/i 4.77dt/o	1.02t
Pc*EuPc*EuPc*	in	12.09			6.36	1.36t
	out	9.15			5.60dt/i 4.77dt/o	1.05t
PcTbPc*TbPc	in	−161.5			−71.16	−9.62
	out		−54.3	−32.6		
PcTbPc*TbPc*	in	−159.4			−73.21 −68.30	−8.94
	out	−51.8	−58.3	−34.78	−33.75/i −15.12/o	−2.64
PcDyPc*DyPc	in	−77.8			−33.52	−4.12
	out		−23.5	−12.8		
PcDyPc*DyPc*	in	−77.4			−35.17 −32.59	−4.04
	out	−22.4	−26.4	−14.5	−14.94/i −5.4/o^c	−0.85
PcHoPc*HoPc	in	n.o.^{d}			−9.0	−0.74t
	out		n.o.^{d}	n.o.^{d}		
PcHoPc*HoPc*	in	−23.2vbr			−9.78 −8.83	−0.70brt
	out	n.o.^{d}	n.o.^{d}	n.o.^{d}	n.o.^{d}	0.34brt^c
PcErPc*ErPc	in	44.9			21.34	3.45t
	out		22.23	15.89		
PcErPc*ErPc*	in	45.5			22.23 20.95^c	3.37t
	out	20.8^c	24.1	17.03	13.16/i 8.55/o	1.72t
PcTmPc*TmPc	in	56.1			26.1	4.05t
	out		26.5	18.80		
PcTmPc*TmPc*	in	56.2			27.18 25.60	3.96t
	out	25.1	28.4	19.90	15.64/i 9.84/o	1.93t

[a] Multiplicities: d = doublet, t = triplet, q = quintet, sx = sextet, m = multiplet or unclear pattern, br = broad or unresolved/obscured pattern. [b] /i, /o = proton directed “inwards”, “outwards”, respectively. [c] Overlapping signals. [d] n.o. = not observed.

could be assigned using COSY and comparison between the two complexes (Table 1). In the case of PcHoPc*HoPc, which was obtained in only very small quantities, no other signals were distinguished. For PcHoPc*HoPc*, one other very broad signal was observed, and it has been assigned to the Pc* (inner) protons. This was unambiguously achieved after the full analysis of the data for remaining late metal ions Dy − Tm (see below) because no other signal is expected to be as far upfield. The unassigned signals are expected to lie among the signals of the alkyl chain protons and those of diamagnetic contaminants such as silicones and chromatography solvent residues, which are very difficult to remove from complexes containing multiple alkyl chains.

So, for series 1, we could conduct an analysis of the LIS (referenced to the diamagnetic yttrium analogues) for the Pc α and Pc β protons in the set Nd, Sm, Eu, Tb, Dy, Er, and Tm, and values for Ho can be included for the Pc* α, OCH$_2$ and CH$_3$ protons. For series 2, more data are available because of the lower symmetry, namely Pc* α (inner Pc* ring) and Pc* α (outer ring), as well as the pairs of nonequivalent OCH$_2$ protons for both the inner and outer rings, and likewise, the inner and outer CH$_3$ protons. In addition, the data for the Pr complex can be included. We have not bothered with analyses of the LIS for the alkyl protons on C2−C7, because the value of the additional information is insignificant, and severe overlap in some cases prevented reliable assignments. The shifts estimated for the intervening protons are listed in the Supporting Information (Table 1S). Assignments for some positions in some complexes required deeper consideration, including those for the Pc* α (outer) protons vs the Pc α protons for the Tb, Dy, Er, and Tm complexes (see Table 1). These are the metals with the largest LIS (and associated broader lines). The short nuclear relaxation times precluded assignments by COSY in some cases, especially when the signals for the more remote protons are so much more intense, creating severe dynamic range problems and spectral artifacts. This is despite using parameters advised for paramagnetic porphyrin complexes.[20]

As an example of the assignment problems, consider the data in Table 1 for PcTmPc*TmPc*. The Pc α protons are readily assigned by integration to the signal at 26.5 ppm in the symmetrical complex PcTmPc*TmPc, but for PcTmPc*TmPc*, there are two signals of very similar line width at 25.1 and 28.4 ppm. The decision on the assignment as shown in Table 1 relied on the following two arguments. First, the Eu complex is a model for the complexes of metals with strong downfield shifts, i.e., the Er and Tm complexes, but has much smaller line widths than the latter pair. For PcEuPc*EuPc*, the signal at 9.20 ppm is easily assigned to the Pc* α (outer) resonance because of the fortunate availability of homoleptic Eu$_2$Pc*$_3$, whose Pc* α (outer) signal appears at 9.15 ppm. On this basis, for the Er and Tm complexes, the less-shifted signals at 20.8 and 25.1 ppm, respectively, can be assigned to the Pc* α (outer) protons. For the Nd$_2$ and Sm$_2$ species, for which the M$_2$Pc*$_3$ were also available, we could also be confident of the assignments. For PcSmPc*SmPc*, the fine structure in the Pc signals makes their discrimination from the Pc* α (outer) signals unambiguous, but now a decision must be made on the order of the α and β Pc signals. In Table 1, we have preferred an assignment which gives the Pc α proton an LIS of −0.56, and the Pc β proton an LIS of −0.35, over the alternative of −0.98 (α) and ~0 (β). An induced shift of zero would be inconsistent with the pattern for the rest of the results matrix. For Eu, the opposite assignment to that in Table 1 gives a Δδ for the β proton of near zero, which would be counter-intuitive. For the Nd complexes, the same ambiguity exists, and we made the assignment on the basis of similarity of the shifts of the Pc* α (outer) and Pc α (necessarily “outer”) in PcNdPc*NdPc*, and similar ratios of $\Delta\delta$ (Pc α)/$\Delta\delta$ (Pc β) for the two types of complex (series 1 and 2). The rest of the assignments followed by ensuring that the larger LIS applies to the Pc α proton. Across the series, this results in the ratio $\Delta\delta$ (Pc α)/$\Delta\delta$ (Pc β) always being >1.48. If the assignments α/β are reversed, ratios varying between 0.51 and 2.09 apply, and this seems most unlikely since the β protons are always farther from the paramagnetic ion, and both contact and dipolar shifts should attenuate with distance (see below).

Analysis of the Induced Shifts. Chemical shift changes induced by the presence of paramagnetic lanthanide ions have been studied for some 30 years. This topic was particularly relevant to the use of LSR in the 1970s and 1980s, before superconducting magnets were in common use. Many authors have used the methods developed by Reilley and co-workers,[13,14] based on theoretical parameters for the effects of the different lanthanide ions deduced by Golding and Bleaney.[10−12] The methods of Reilley are explained clearly in a series of papers by Sherry and co-workers.[16,17] More recently, Bünzli, Piguet and others[21−25] have revisited these treatments and shed considerable light on their use in the structural analysis of lanthanide complexes of nonaromatic N-ligands. In structural studies using LSR, corrections to the LIS models may have to be made for the effects of incomplete complexation and dynamic behavior, whereas we are dealing with irreversibly coordinated lanthanide ions (except perhaps for Pr).

The LIS ($\Delta\delta$, calculated here by reference to the diamagnetic di-yttrium complexes) for each proton are partitioned into through-bond (contact) and through-space (pseudo-contact or dipolar) contributions

$$\Delta\delta_{\mathrm{obs}} = \Delta\delta_{\mathrm{c}} + \Delta\delta_{\mathrm{d}} \qquad (1)$$

The former term is directly related to spin delocalization via covalency and is proportional to the spin expectation value, usually denoted $\langle S_z\rangle_j$, of the particular lanthanide ion, and the electron−nuclear hyperfine coupling constant F_i. The values of $\langle S_z\rangle$ represent the projection of the total electron spin magnetization of the lanthanide ion on the direction of the external magnetic field. The dipolar shift results from through-space interaction and is a function of the magnetic anisotropy and geometry of the complex. Its value depends on the magnetic constant D (sometimes denoted C^D or D_z) characteristic of each ion, the crystal field coefficient, and a geometric factor.[16] In the case of axial symmetry (as applies here), there is only one crystal field parameter, and for a particular nucleus i, and lanthanide j, the equation reduces to

$$\Delta\delta_{\mathrm{obs}} = \Delta\delta_{ij} = F_i\langle S_z\rangle_j + G_i{\cdot}A_2{}^0\langle r^2\rangle{\cdot}D_j \qquad (2)$$

where the temperature dependence has been included in F_i (T^{-1}) and G_i (T^{-2}). The crystal field parameter $A_2{}^0\langle r^2\rangle$ measures the magnitude of the interaction between a given lanthanide j and the ligand donor atoms, and G_i is the geometric factor of nucleus i, related to the angle θ_i between the Ln-H$_i$ vector and the principal axis of the complex, and the internuclear distance r_i by

$$G_i = (3\cos^2\theta_i - 1)r_i^{-3}$$

Equation 2 can be used to extract the coefficients F_i (representing the sensitivity of the shift of proton i to contact interaction with lanthanide j), and $G_i{\cdot}A_2{}^0\langle r^2\rangle$ (the sensitivity to dipolar influences) by transforming to equations (3) and (4), provided certain conditions apply. These are: (i) the series of complexes is isostructural; (ii) the temperature is constant (in our case, 292 ± 1 K); and (iii) the hyperfine coupling constant F_i and the crystal-field parameter $A_2{}^0\langle r^2\rangle$ are constant across the series. The former equation is more precise when the total induced shift is largely contact in origin, and the latter when the shifts are dominated by the dipolar terms[13,14]

$$\Delta\delta_{ij}/D_j = F_i\langle S_z\rangle_j/D_j + G_i{\cdot}A_2{}^0\langle r^2\rangle \qquad (3)$$

$$\Delta\delta_{ij}/\langle S_z\rangle_j = F_i + G_i{\cdot}A_2{}^0\langle r^2\rangle{\cdot}D_j/\langle S_z\rangle_j \qquad (4)$$

The values of S_j and D_j have been calculated from theory, are generally assumed to be temperature-independent near 300 K, and are tabulated in a number of papers.[10−12] We used the values of Golding and co-workers.[11,12] Equations 3 and 4 have been used to analyze LIS in a large number of LSR studies, but it has been appreciated recently that the inherent assumptions simply do not apply in many cases.[21−24]

Of course, there is a further complication in treating our systems, the presence of two lanthanide ions in the complexes. Piguet and Bünzli[21,23] have modified the treatment described above to apply to dimetallic triple helicate complexes, and note that a single F_i term should suffice where the Fermi contact contribution involves through-bond interactions with only one center, as in their nonaromatic complexes. Moreover, in a case where there is no magnetic coupling between the two Ln(III) ions, the geometric factors contributed by the two ions at a given H$_i$ can be considered as additive. Our complexes, however, may conceivably represent a different situation, because (i) the central phthalocyanine ring shares bonding with two lanthanides; (ii) the metal ions are situated ≤ 3.8 Å apart and (iii) the ligands are extensively conjugated. Notwithstanding these potential interferences, we show below that our LIS generally behave typically when subjected to the usual treatments, and indeed reinforce a growing body of recent data which have challenged the validity of the underlying assumptions of eqs 3 and 4.

The LIS in rare earth phthalocyanine complexes could potentially involve both contact and dipolar contributions. At the outset, it seemed reasonable to assume that contact effects are negligible in the alkoxy side chains because even the OCH$_2$ protons are removed by 8 bonds from the lanthanide, but we return to this assumption below. Contact interactions could still be important for the protons directly attached to the Pc and Pc* rings. To begin the discussion, we note that all the $\Delta\delta_{ij}$ values have the same signs as their respective D_j coefficients, and thus, the LIS are, to a first approximation, dominated by the dipolar contributions. Buchler et al. were able to rely on this assumption in their studies of triple-decker M$_2$(OEP)$_3$, but their series was limited to the early metals Ce, Pr, Nd, Sm, and Eu.[19] Plotting $\Delta\delta_{ij}$ vs the dipolar term D_j is a simple way to check for the intrusion of contact dependence. As illustrations, examples of such plots for each of series 1 and 2 are shown in Figures 3 and 4, respectively. These examples were chosen as they include data for Ho complexes. The plots for all other positions in both series give similar results. The plots apparently exhibit good linearity when the points for Tb complexes are omitted. A deviation for Tb is interesting, as both Tb and Dy have $\langle S_z\rangle_j$ and D_j values which are large and negative. This draws attention to a discontinuity in the series, which is explored below.

Returning now to eqs 3 and 4, correlations were explored for the sets of protons Pc* α, Pc α, Pc β, OCH$_2$ and CH$_3$ for series 1, and the protons Pc* α (inner), Pc* α (outer), Pc α, Pc β, OCH$_2$ (4 sets, 2 pairs of nonequivalent inner and outer ring protons), CH$_3$ (inner) and CH$_3$ (outer) for series 2. As noted

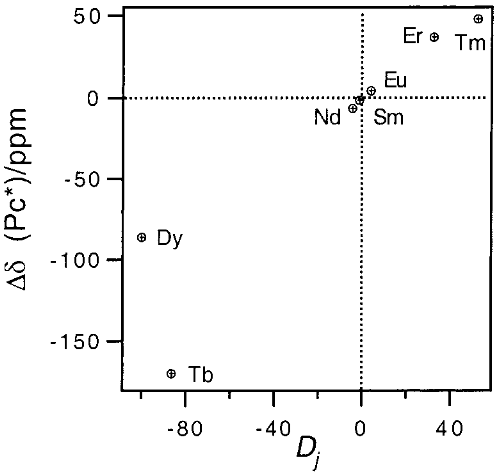

Figure 3. Plot of the LIS of Pc* α protons vs dipolar parameter D_j for series 1.

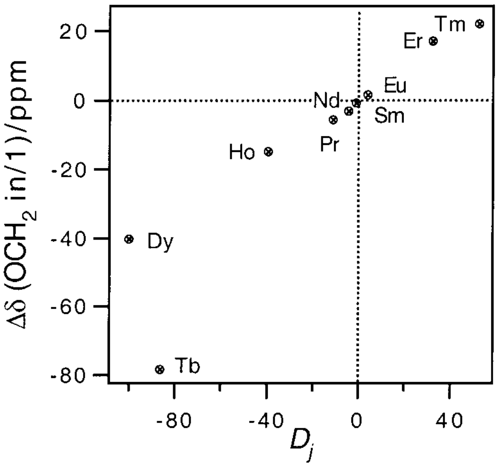

Figure 4. Plot of the LIS of OCH_2 (inner ring) protons vs dipolar parameter D_j for series 2.

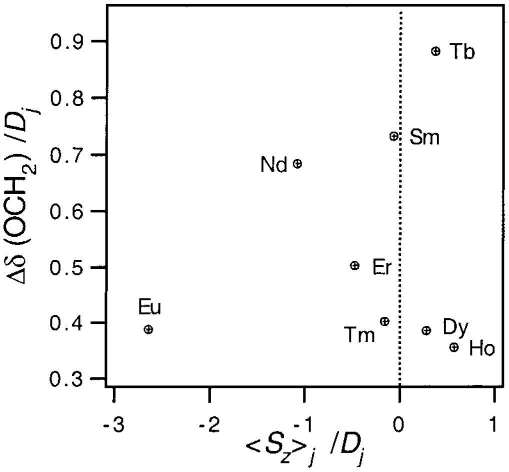

Figure 5. Plot according to eq 3 for the OCH_2 protons for series 1.

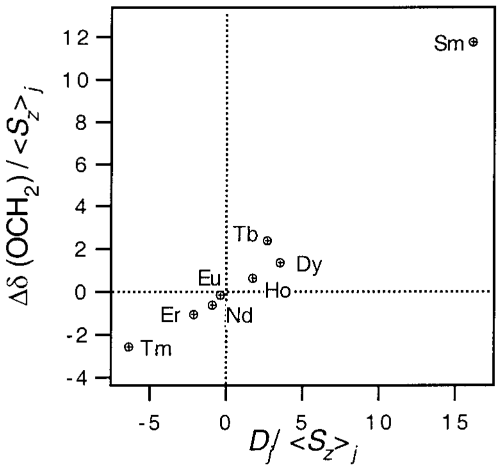

Figure 6. Plot according to eq 4 for the OCH_2 protons for series 1.

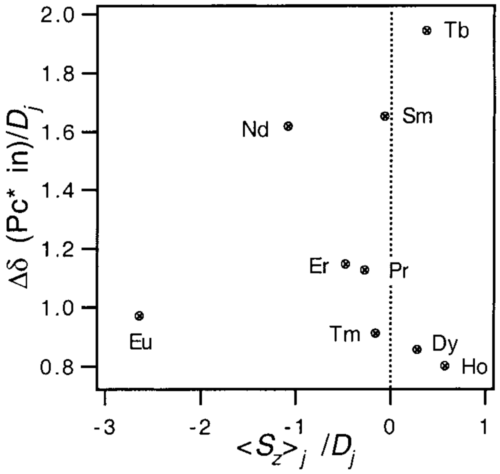

Figure 7. Plot according to eq 3 for the Pc* α (inner ring) protons for series 2.

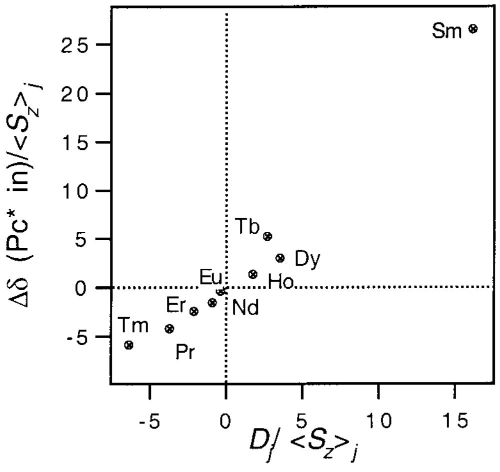

Figure 8. Plot according to eq 4 for the Pc* α (inner ring) protons for series 2.

above, we would expect a better correlation for plots according to eq 4 because of the dominance of dipolar contributions, and this is indeed the case for all positions in both series. Typical examples are shown in Figures 5 and 6 for the OCH_2 protons in series 1 and Figures 7 and 8 for the Pc* (inner) protons for series 2. The analogous plots for all other positions for both series have similar appearances. The plots according to eq 4 (e.g., Figures 6 and 8) exhibit fair correlations, again indicating predominance of the dipolar mechanism. The dipolar terms $G_i \cdot A_2^0\langle r^2\rangle$ are positive in all positions. The plots according to eq 3 appear at first sight to give very poor correlations, but upon closer examination, the data split into two groups. For the elements Nd, Sm, Eu, and Tb, a positive slope F_i can be discerned, while for the heavier elements Dy−Tm, a smaller, negative value gives a better fit. The one outlier is Pr, which clearly fits better into the latter group, despite its early position in the lanthanide series. Because of this curious fact, we omitted the data for the Pr complex from this treatment. Such light/

heavy divisions have been found frequently in the past for a number of systems, and have often been interpreted as reflecting a significant change in geometry or a change in coordination number.[14,16−18,21−24] More recently, other explanations have gained currency.[21−24] The exact position of the break in the series varies among different complex types, often occurring around gadolinium (the "gadolinium break"[23]), but here it lies between Tb and Dy.

Although the plots according to eq 3 show the light/heavy division rather clearly because of the change in sign of F_i, it can also be discerned more subtly in the eq 4 plots, e.g., see Figures 6 and 8. The points for Dy−Tm form a subset with good linearity, and a lesser slope than for the complete set. This discontinuity between Tb and Dy offers a solution to the apparent mis-fit of the Tb points in the previously described plots of $\Delta\delta_{ij}$ vs the dipolar parameter D_j (Figures 3 and 4). So it appears that the data fit well a model with two sets of F_i, $G_i{\cdot}A_2^0\langle r^2\rangle$ values for each proton position in each series. The light elements have a positive value for F_i, and the heavy ones have a negative F_i. This split was performed for all the data, and two values for F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ were deduced by linear regression treatment according to eqs 5 and 6, for each type of proton. The values for $G_i{\cdot}A_2^0\langle r^2\rangle$ were obtained from the slopes of the $\Delta\delta_{ij}/\langle S_z\rangle_j$versus $D_j/\langle S_z\rangle_j$ plots, and the values of F_i from the plots of $\Delta\delta_{ij}/D_j$ versus $\langle S_z\rangle_j/D_j$. The former plots always gave better correlations than the latter, as expected when dipolar shifts dominate. There was also the expected attenuation of the magnitudes of F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ for protons farther out from the core. The precision of determination of the slopes by linear regression was always better than that for the intercepts, which is the basis of using eqs 3 and 4. Even using only the slopes, the estimated relative errors in F_i become very large (> 100%) as the magnitude of the coefficient diminishes.

By substituting these derived values back into eq 4, one can obtain $\Delta\delta_{\mathrm{calc}}$ values, and compare them with the observed LIS for each position by plotting the two according to eq 5[14]

$$\Delta\delta_{\mathrm{calc}} = M(\Delta\delta_{\mathrm{obs}}) + C \tag{5}$$

For all positions, the two are well-correlated, but the calculated LIS are systematically low (in absolute terms) for all positions and over all metals. For example, for Pc* α (series 1), $M = 0.910$ (± 0.017), $C = +1.5$ (± 1.3), $r = 0.9991$. Having reached this impasse, we turned to another method of treating the data, namely the pseudoinverse method of solving overdetermined sets of linear equations in order to get the most unbiased solution (using the application MATLAB). The input matrices are the sets of LIS values and the known D_j and $\langle S_z\rangle_j$ values (divided as above into the "light" and "heavy" data). The values for F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ agreed approximately with those emerging from the graphical method, but $\Delta\delta_{\mathrm{calc}}$ derived from the matrix method now agrees very well with $\Delta\delta_{\mathrm{obs}}$, the slope M being very close to 1, and intercept C very close to 0. For example, for Pc* α (series 1), $M = 1.003$ (± 0.017), $C = -0.00$ (± 0.72), $r = 0.9998$. This can be compared with the values derived above for the same proton position. The sets of F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ so derived are collected in Table 2, and the $\Delta\delta_{\mathrm{calc}}$ and $\Delta\delta_{\mathrm{obs}}$ values for the whole set are compared in the Supporting Information (Table 2S). The pseudoinverse method does not generate estimated errors in F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$. We have used as an overall measure of the deviation between $\Delta\delta_{\mathrm{calc}}$ and $\Delta\delta_{\mathrm{obs}}$, the relative error R, derived by

$$R = [(|\Delta\delta_{\mathrm{obs}} - \Delta\delta_{\mathrm{calc}}|)/\Sigma(|\Delta\delta_{\mathrm{obs}}|)] \times 100 \tag{6}$$

TABLE 2: Contact and Dipolar Coefficients Derived by the Pseudoinverse Method

		Nd−Tb			Dy−Tm		
series	proton	F_i	$G_i{\cdot}A_2^0\langle r^2\rangle$	R/%	F_i	$G_i{\cdot}A_2^0\langle r^2\rangle$	R/%
1	Pc*	0.316	1.851	0.37	−0.25	0.93	3.8
	Pc α	0.131	0.681	0.34	−0.097	0.35	4.1
	Pc β	0.103	0.432	0.30	−0.029	0.21	3.0
	OCH_2[a]	0.160	0.825	0.32	−0.10	0.41	3.6
	CH_3[a]	0.0186	0.118	0.52	−0.018	0.057	4.0
2	Pc* in[a]	0.304	1.833	0.44	−0.26	0.93	3.7
	Pc* out	0.125	0.647	0.53	−0.090	0.33	3.3
	Pc α	0.142	0.732	0.27	−0.12	0.38	4.2
	Pc β	0.111	0.455	0.31	−0.042	0.24	3.6
	OCH_2 in/1[a]	0.159	0.849	0.55	−0.11	0.43	3.9
	OCH_2 in/2[a]	0.147	0.796	0.62	−0.096	0.40	3.8
	OCH_2 out/in	0.0601	0.423	0.89	−0.064	0.21	4.1
	OCH_2 out/out	0.0287	0.214	0.71	−0.038	0.11	4.0
	CH_3 in[a]	0.0173	0.110	0.65	−0.018	0.056	3.8
	CH_3 out[a]	0.0055	0.0393	1.3	−0.0067	0.019	3.6

[a] Datum for Ho included.

The R values are included in Table 2, and were used to assign the number of significant figures for the F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ values. This procedure does not, of course, generate separate estimates of the errors in F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$. Clearly, the early elements give much better agreement. This might be thought to be because of the absence of a datum for Ho in several cases, but the R values are hardly different whether Ho is present or absent. In Table 2S, we also show that the fit for the Pr complex is considerably better when the $\Delta\delta_{\mathrm{calc}}$ values are derived from the F_i, $G_i{\cdot}A_2^0\langle r^2\rangle$ parameters of the heavy lanthanides, confirming the anomalous nature of the Pr complex.

The conclusion that these abrupt changes in mid-series are due to gross structural changes is rather unlikely. UV/visible spectroscopy would be expected to reveal such changes, yet there is a smooth progression in the energies of the Q-band absorptions across both series 1 and 2, which is easily attributable to the gradual effects of the lanthanide contraction on the inter-ring electronic interactions.[8] We must therefore look elsewhere for reasons for the discontinuity. In 1982, Reuben introduced another method of treating LIS data, by factoring out the crystal field coefficient $A_2^0\langle r^2\rangle$ by comparing the shifts of two nuclei i and k in an isostructural series.[26] This procedure was developed further by Geraldes and co-workers[24] and Piguet and co-workers,[21−23] according to the equations below

$$\Delta\delta_{ij} = F_i\langle S_z\rangle_j + G_i{\cdot}A_2^{\;0}\langle r^2\rangle{\cdot}D_j$$

$$\Delta\delta_{kj} = F_k\langle S_z\rangle_j + G_k{\cdot}A_2^{\;0}\langle r^2\rangle{\cdot}D_j$$

$$\Delta\delta_{ij}/\langle S_z\rangle_j = (F_i - F_k{\cdot}R_{ik}) + R_{ik}{\cdot}\Delta\delta_{kj}/\langle S_z\rangle_j \tag{7}$$

where $R_{ik} = G_i/G_k$

If the data for all possible combinations i,k are examined, significant changes in geometry would be revealed by the continued presence of a discontinuity (two different R_{ik} values), whereas significant changes in the hyperfine coupling constant *may* be apparent by nonlinearity or the existence of two near-parallel lines. Recently, these methods have been applied to N,O-macrocycles,[25] cryptates[24] and supramolecular dimetallic complexes.[21−23] It is very opportune to subject the data from our aromatic triple-decker sandwich complexes (which differ greatly from the above types in both electronic and structural properties) to the same treatment. Again, we proceed under the assumption that the presence of two metal ions will not interfere with the treatment, as this appeared justified so far.

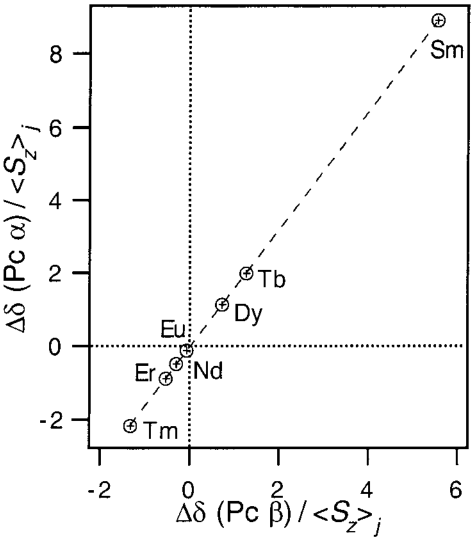

Figure 9. Plot of $\Delta\delta$ (Pc α)/$\langle S_z\rangle_j$ vs. $\Delta\delta$ (Pc β)/$\langle S_z\rangle_j$ for series 1 according to eq 7.

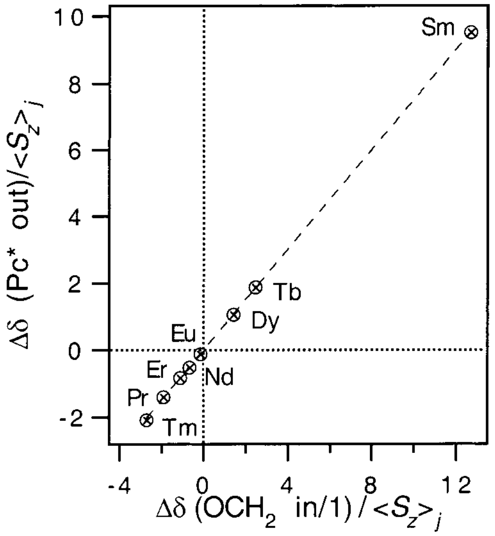

Figure 10. Plot of $\Delta\delta$ (Pc* out)/$\langle S_z\rangle_j$ vs. $\Delta\delta$ (OCH_2 in/1)/$\langle S_z\rangle_j$ for series 2 according to eq 7.

All our data for both series were subject to plotting according to eq 7. As typical examples, we show in Figures 9 and 10 the respective results for comparison of Pc α versus Pc β in series 1 and Pc* (outer) vs OCH_2 (inner/1) in series 2. The plots for all other combinations in both series are comparable, mostly giving correlation coefficients >0.999. The only exceptions are those where the shifts are relatively small, because the Sm data point becomes increasingly subject to error due to its weak paramagnetism and hence very small $\langle S_z\rangle_j$ value. In such cases, we have omitted the point due to Sm, which improves the correlation. Otherwise, all the metals fall very close to the lines. It must be pointed out that the use of this equation for series 2 is not strictly justified because the lower symmetry means the two metal sites are not identical. However, the fact that the correlations are no worse than those for series 1 appears to indicate that the crystal field coefficients of the Pc and Pc* ligands must be nearly identical. This is a reasonable expectation, given the minor differences between the Pc and the Pc* ligands. The derived slopes, intercepts and correlation coefficients for a selected set of comparisons for series 1 are shown in Table 3, and the rest of the derived values for both series are collected in the Supplementary Information (Table 3S). The fact that all our data fit eq 7 without breaking into the light/heavy pattern clearly confirms the intuitive presumption that there is no drastic structural change across the series.

TABLE 3: Selected Set of Data from Plots of $\Delta\delta_{ij}/\langle S_z\rangle_j$ vs $\Delta\delta_{kj}/\langle S_z\rangle_j$ for Series 1 complexes according to Eq 7

parameter	Pc*/Pc α	Pc*/Pc β	Pc*/OCH_2	Pc*/CH_3
R_{ik} (slope)	2.92(4)	4.70(7)	2.245(2)	16.50(9)
$F_i - F_k{\cdot}R_{ik}$ (intercept)	0.06(15)	−0.08(15)	−0.029(8)	0.03(6)
correlation coeff, r	0.9995	0.9995	1.0000	0.9999

We conclude that the discontinuity in our data is due to variation in the crystal field coefficients $A_2^0\langle r^2\rangle$ and the hyperfine coupling constants F_i. Simulation of the slopes and intercepts of eq 7 using our previously derived F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ values (Table 2) gives good agreement in most positions. By analogy with the recent work of Rigault and Piguet,[22,23] we have calculated from the data in Table 2 the mean ratio of the crystal field coefficients for the two sets Nd−Tb and Dy−Tm. These are remarkably consistent across all positions and for both series, being 2.00(4) for series 1 and 1.98(5) for series 2. The situation for the hyperfine coupling constants is obscured in our complexes by the fact that the intercepts for plots of eq 7 are uniformly very close to zero, with correspondingly large relative errors. So despite the rather dramatic changes in F_i between early and late metals (notably a change in sign), the effects on the eq 7 plots are negligible. Our data show that the crystal-field independent approach can sometimes be very insensitive to changes in the Fermi contact terms. This was also the case for the triple helicates of Rigault and Piguet.[22,23] The discontinuity between Tb and Dy is due to the specific electronic properties of the particular lanthanide ions, rather than to a gross structural change. The fact that the break in our data occurs after Tb is somewhat unusual because specific effects due to the half-filled f shell normally manifest themselves appropriately at gadolinium. However, our data seem quite clear on this point. As a tentative explanation of this fact, we propose that it could arise from the superimposition of two other influences on the already complex electronic effects. The first is a (relatively minor) geometric effect due to the steady contraction of ionic radius and inter-macrocycle distance. This should affect the average skew angle between the macrocycle axes, as well as the degree of doming of the outer rings. Second, for the strongly paramagnetic Tb(III) and Dy(III) ions, perhaps the magnetic exchange in these dimetallic complexes cannot be completely ignored (see below).

The peculiarity of Pr can be accounted for by the premise that the coordination of the phthalocyanine ligands with this large metal ion near the start of the series is rather weak. There is chemical evidence to support the fact that Pr occupies a unique position in our series. The difficulty in preparing and purifying the triple-decker phthalocyanine complexes of Pr(III) can be rationalized as follows. Along with the increase of rare earth ionic size from Lu to La, the yield of bis(phthalocyaninato) rare earth obtained by either the condensation of dilithium phthalocyanine $Li_2(Pc)$ or the cyclotetramerization of dicyanobenzene in the presence of rare earth metal salts gradually decreases.[27] In the case of the naphthalocyaninato rare earth double-deckers $M[Nc(^tBu)_4]_2$, the double-decker of lanthanum(III), which has the largest ionic radius of the rare earths, decomposes within a few days even in the solid state under N_2.This is despite (for this series) an increase in the reaction yield with the increase of rare earth ionic size from Lu to La.[28] As described in our previous paper concerning the synthesis of these phthalocyaninato rare earth triple-deckers,[8a] the complexes are more easily prepared for the late rare earths with smaller ionic size. It should

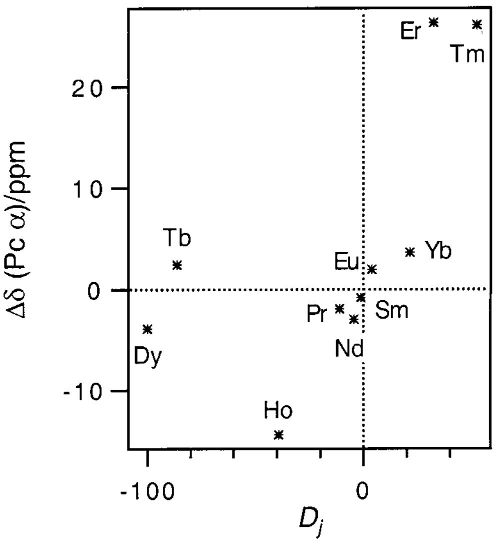

Figure 11. Plot of LIS for Pc α protons in double-decker complexes $[n\text{-}Bu_4N]^+[MPc_2]^-$ (from Konami et al., ref 3) vs dipolar parameter D_j.

be pointed out that due to the increased ring−ring distance in the triple-deckers compared with that of double-deckers, the stability of triple-decker rare earth phthalocyanines should be worse than that of the corresponding double-deckers. Although the dissociation of bis(phthalocyanine)s with early rare earths (La, Ce, and Pr) was not noticed so far, the instability of PcPrPc*PrPc* is quite reasonable. This conclusion is further supported by the dissociation of the lanthanum analogue.[8b]

We now turn to the possibility of deducing geometrical information from the LIS. Because of the angle- and distance dependence of the dipolar contribution to the total LIS, separation of this term has often be used to determine the average solution geometries of complexes. Normally, one would start with some reliable geometric parameter established from a crystal structure, and attempt to model the rest of the molecule from the shift ratios. In the present case, there is very little information available. There is no published crystal structure of an analogue of series 1 or 2, nor even of any homoleptic M_2Pc_3 triple-decker in which M is a rare earth ion. The only relevant structures are those of the mixed porphyrin-Pc complexes (Pc)Ce[T(4-OCH_3)PP]Ce(Pc),[29] (TPP)Ce[Pc(OMe)$_8$]Ce(TPP),[29] and [T(4-OCH_3)PP]Nd(Pc)Nd(Pc).[30] These structures show that the internal ring in a symmetrical complex is planar, while the outer rings are domed. Moreover, the metal-nitrogen distances to the internal ring are expected to be longer than those to the outer rings. However, there are not enough data to be able to compare early and late metals, nor to predict the degree of eclipsing between the macrocycles. In considering whether we could use our data to determine some geometries, it rapidly became evident that there are presently too many unknowns to tackle this problem reliably, and we will have to wait for more structural data, or more NMR studies of similar systems.

Last, we compare our results with the only published study of similar sandwich Pc complexes, in which Konami et al. studied the NMR effects of the paramagnetic metal ions in the series $[n\text{-}Bu_4N]^+[MPc_2]^-$, covering the array of metals from Pr to Lu.[3] For the unsubstituted Pc ligand, of course there are only two sets of induced shifts, namely $\Delta\delta$ (Pc α) and $\Delta\delta$ (Pc β). Because of the paucity of studies in this field, we have examined their data by the same methods we applied to ours. To illustrate the differences, Figure 11 shows a plot of $\Delta\delta$ (Pc α) vs D_j. Clearly, the correlation of the whole set is poor, indicating that the contact contribution may be much stronger in these complexes. The authors' analysis by a least-squares method generated the values (over the whole series of metals) of $F_i = -0.659$, $G_i{\cdot}A_2^0\langle r^2\rangle = 0.284$ (for Pc α) and $F_i = -0.360$, $G_i{\cdot}A_2^0\langle r^2\rangle = 0.143$ (for Pc β).[3] We obtain almost identical values using our MATLAB method. The agreement between observed and calculated LIS using these values is much worse than for our data, and the divergence is particularly bad for Ho. The R values for the α and β protons are 68 and 66%, respectively. The surprising point from this analysis is the predominance of the contact term and the relative insensitivity to dipolar effects compared with our data for similar positions, e.g. for Pc α in our series 1, $F_i = 0.131$, $G_i{\cdot}A_2^0\langle r^2\rangle = 0.681$ (early metals) and $F_i = -0.097$, $G_i{\cdot}A_2^0\langle r^2\rangle = 0.346$ (late metals). However, the inclusion of the data for all metals clearly leads to very large uncertainties, given the scatter of the points.

Careful examination of the plots according to eqs 3 and 4 does actually allow a qualitative separation into similar groups as for our complexes. For eq 3, the group Nd, Sm, Eu deviate strongly from the set Tb−Yb (with Pr fitting in the *latter* group, and Ho most deviant), while for eq 4, the same groupings apply, except this time Yb appears to deviate (Supplementary Information, Figures 1S−3S). The structural situation is simpler in these homoleptic double-deckers of unsubstituted Pc, with only one metal ion to consider. As noted above, our shifts are the result of sums/convolutions of the effects of two metal ions, and particularly for series 2, the nonaxial symmetry is lower. Examination of the Konami data according to eq 7 gives a reasonable straight line, with $R_{ik} = 1.79(2)$, intercept = −0.06(5) ($r = 0.9993$), and the point for Ho is again the most displaced from the line. Once more the complexes appear (as expected) to be isostructural, but the scatter of the results from correlations according to eqs 3 and 4 seems to indicate that there must be significant changes in both the hyperfine coupling constants and the crystal-field coefficients across the series, leading to unpredictable swings in their combined effects. It is noteworthy that the intercept for eq 7 is virtually zero (as for all our results), and also that the R_{ik} is not dissimilar to that found for the comparable Pc α/Pc β combination in our series 1 complexes (1.79 vs 1.61). Moreover, it is remarkable and reassuring that the peculiar situation of praseodymium is revealed for the double-deckers as well, and that there is a break in the middle of the series. For Konami's complexes, the discontinuity appears to be in its more logical position between Eu and Tb, perhaps due to the fact that only one metal ion is present in these double-deckers. Further enlightenment may occur as more systems are studied by similar methods, as we will be doing in the near future.

3. Conclusions

This study represents the first attempt to define and compare the NMR effects of the lanthanide(III) ions in triple-decker phthalocyaninato complexes. A large body of data was obtained because of the availability of two/three series of mixed Pc/Pc* complexes. Self-consistent assignments were made based on the symmetries of the three types of complexes, and the LIS values were used to study the separation into contact and dipolar effects of the paramagnetic ions. In the series of unsymmetrical complexes PcMPc*MPc*, the effects of the octakis(octyloxy) substitution are detectable in the NMR shifts. The data for the praseodymium complex are aberrant, and we note that this complex is the least stable of the set, because of the large ionic radius of Pr(III). The complexes of the early metals Nd, Sm, Eu, and Tb are well-behaved and the LIS correlate well with positive contact and dipolar sensitivities. However, there is a clear distinction between these metals and the group Dy, (Ho), Er, and Tm, which demands a change of sign of the contact term, and a marked diminution of the dipolar sensitivity. The attenuation of the contact term is surprisingly gradual, and its effects are discernible in the data even over >4 bonds. Treatment by crystal-field independent methods showed that the break in the middle of the series of lanthanides is not due to gross geometrical changes, but rather to a combination of changes in the Fermi contact and crystal-field coefficients due to the particular electronic properties of the lanthanide(III) ions. The contraction in ionic radius across the series and the effects of magnetic interaction between the metal ions may superimpose complications on these electronic effects, leading to the appearance of the mid-series break between Tb and Dy. It has been noted that there is no magnetic coupling at room temperature between lanthanide ions at distances greater than 4 Å.[31] From crystal structures of related complexes, the intermetallic distances in our triple-deckers are expected to be less than this, even below 3.5 Å.[29,30] It is therefore conceivable that there is magnetic coupling between the ions in our sandwich triple-deckers because there is a precedent in a Gd,Gd triply bridged complex which is expected to have a similar metal−metal distance.[32] Further investigations of the magnetic moments of triple-decker macrocyclic sandwiches are definitely warranted but are beyond the scope of our present work. Our results confirm the findings of a number of other workers using very different ligands, that the assumptions of the crystal-field dependent treatment of LIS data must be applied cautiously. Moreover, our findings complement those from a more limited set of data for double-decker Pc complexes,[3] and both studies indicate unique LIS behavior for Pr(III) in these sandwich complexes, probably related to the instability of sandwich complexes of the larger rare earth ions.

4. Experimental Section

The compounds were available from our preparative studies.[8] The compound PcPrPc*PrPc* could not be entirely separated from the symmetrical analogue PcPrPc*PrPc, and both these complexes were subject to demetalation in solution. ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer in $CDCl_3$ solutions at 19 ± 1 °C.

Acknowledgment. We thank the Visiting Scholar Foundation of the Key Laboratory in Shandong University, the State Educational Ministry of China, the Natural Science Foundation of China (Grant No. 29701002), the Natural Science Foundation of Shandong Province (Z99B03), the Science Committee of Shandong Province, Shandong University and the Australian Research Council for financial support and QUT for a Postdoctoral Fellowship for J.J., and Dr M. Selby for assistance with the MATLAB calculations.

Supporting Information Available: Tables 1S−3S, showing the complete data matrix of chemical shifts, the complete set of derived contact and dipolar terms and comparison of calculated and observed LIS, and the complete set of results for the treatment of our data according to eq 7, and Figures 1S−3S showing plots of the data of Konami et al. (ref 3) according to eqs 3 and 4 for the Pc α protons, and according to eq 7 for the pair Pc α/Pc β (the point for Sm is omitted to allow clearer display of the remaining points) (12 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Leznoff, C. C.; Lever, A. B. P., Eds.; *Phthalocyanines: Properties and Applications*; VCH: New York, Vol. 1, 1989; Vol. 2, 1993; Vol. 3, 1993; Vol. 4, 1996. (b) Kadish, K. M.; Smith, K. M.; Guilard, R., Eds.; *The Porphyrin Handbook*; Academic Press: San Diego, 2000; Vols. 1−10.

(2) (a) Buchler, J. W.; Ng, D. K. P. In *The Porphyrin Handbook*; Kadish, K. M.; Smith, K. M.; Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 3, 245−294. (b) Ng, D. K. P.; Jiang, J. *Chem Soc. Rev.* **1997**, *26*, 433−442. (c) Jiang, J.; Kasuga, K.; Arnold, D. P. In *Supramolecular Electroactive and Photosensitive Materials*, Nalwa, H. S., Ed.; Academic Press: San Diego, **2001**, 113−210.

(3) Konami, H.; Hatano, M.; Tajiri, A. *Chem. Phys. Lett.* **1989**, *160*, 163−167.

(4) (a) Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 1287−1291. (b) Pondaven, A.; Cozien, Y.; L'Her, M. *New J. Chem.* **1992**, *16*, 711. (c) Guyon, F.; Pondaven, A.; Guenot, P.; L'Her, M. *Inorg. Chem.* **1994**, *33*, 4787−4793. (d) Jiang, J.; Liu, R. C. W.; Mak, T. C. W.; Chan, T. D. W.; Ng, D. K. P. *Polyhedron* **1997**, *16*, 515−520. (e) Toupance, T.; Ahsen, V.; Simon, J. *J. Am. Chem. Soc.* **1994**, *116*, 5352−5361. (f) Toupance, T.; Bassoul, P.; Mineau, L.; Simon, J. *J. Phys. Chem.* **1996**, *100*, 11 704−11 710.

(5) Takahashi, K.; Shimoda, J.; Itoh, M.; Fuchita, Y.; Okawa, H. *Chem. Lett.* **1998**, 173−174.

(6) (a) Jiang, J.; Lau, R. L. C.; Chan, D.; Mak, T. C. W.; Ng, D. K. P. *Inorg. Chim. Acta* **1997**, *255*, 59−64. (b) Jiang, J.; Liu, W.; Law, W.-F.; Lin, J.; Ng, D. K. P. *Inorg. Chim. Acta* **1998**, *268*, 49−53.

(7) Arnold, D. P.; Jiang, J. *Chem. Lett.* **1999**, 483−484.

(8) (a) Liu, W.; Jiang, J.; Pan, N.; Arnold, D. P. *Inorg. Chim. Acta* **2000**, *310*, 140−146. (b) Jiang, J. unpublished results.

(9) Horrocks, W. DeW.; Sipe, III, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 6800−6804.

(10) Bleaney, B. *J. Magn. Res.* **1972**, *8*, 91−100.

(11) Golding, R. M.; Halton, M. P. *Aust. J. Chem.* **1972**, *25*, 2577−2581.

(12) Golding, R. M.; Pyykkö, P. *Mol. Phys.* **1973**, *26*, 1389−1396.

(13) Reilley, C. N.; Good, B. W.; Desreux, J. F. *Anal. Chem.* **1975**, *47*, 2110−2116.

(14) Reilley, C. N.; Good, B. W.; Allendoerfer, R. D. *Anal. Chem.* **1977**, *48*, 1446−1458.

(15) Reuben, J.; Elgavish, G. A. *J. Magn. Res.* **1980**, *39*, 421−430.

(16) Sherry, A. D.; Singh, M.; Geraldes, C. F. G. C. *J. Magn. Res.* **1986**, *66*, 511−524.

(17) Geraldes, C. F. G. C.; Sherry, A. D.; Kiefer, G. E. *J. Magn. Res.* **1992**, *97*, 290−304.

(18) Babecki, R.; Platt, A. W. G.; Fawcett, J. *J. Chem. Soc., Dalton Trans.* **1992**, 675−681.

(19) (a) Buchler, J. W.; Kihn-Botulinski, M.; Löffler, J.; Wicholas, M. *Inorg. Chem.* **1989**, *28*, 3770−3772. (b) Buchler, J. W.; Löffler, J.; Wicholas, M. *Inorg. Chem.* **1992**, *31*, 524−526.

(20) Walker, F. A.; Simonis, U. In *Biological Magnetic Resonance, Vol. 12: NMR of Paramagnetic Molecules*; Berliner, L. J., Reuben, J., Eds.; Plenum Press: New York, 1993; pp 133−274.

(21) Rigault, S.; Piguet, C.; Bünzli, J.-C. G. *J. Chem. Soc., Dalton Trans.* **2000**, 2045−2053.

(22) Rigault, S.; Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4587−4600.

(23) Rigault, S.; Piguet, C. *J. Am. Chem. Soc.* **2000**, *122*, 9304−9305.

(24) Platas, C.; Avecilla, F.; de Blas, A.; Geraldes, C. F. G. C.; Rodríguez-Blas, T.; Adams, H.; Mahía, J. *Inorg. Chem.* **1999**, *38*, 3190−3199.

(25) Ren, J.; Sherry, A. D. *J. Magn. Res.* **1996**, *111B*, 178−182.

(26) Reuben, J. *J. Magn. Res.* **1982**, *50*, 233−236.

(27) (a) Iwase, A.; Harnoode, C.; Kameda, Y. *J. Alloys Compd.* **1993**, *192*, 280. (b) Liu, W.; Jiang, J.; Du, D.; Arnold, D. P. *Aust. J. Chem.* **2000**, *53*, 131−135.

(28) Jiang, J.; Liu, W.; Poon, K.-W.; Du, D.; Arnold, D. P.; Ng, D. K. P. *Eur. J. Inorg. Chem.* **2000**, 205−209.

(29) Chabach, D.; Lachkar, M.; De Cian, A.; Fischer, J.; Weiss, R. *New J. Chem.* **1992**, *16*, 431−433.

(30) Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1986**, *25*, 2107−2108.

(31) Elhabiri, M.; Scopelliti, R.; Bünzli, J.-C. G.; Piguet, C. *J. Am. Chem. Soc.* **1999**, *121*, 10 747−10 762.

(32) Costes, J.-P.; Dahan, F.; Dupuis, A.; Lagrave, S.; Laurent, J.-P. *Inorg. Chem.* **1998**, *37*, 153−155.