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Bis(phthalocyaninato)gadolinium(III) Hexacyanobutadienide(1−), $[GdPc_2]^+[C_4(CN)_6]^-$. An Electron Transfer Salt with Four Paramagnetic Sites

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Metallophthalocyanines, MPc (H_2Pc = phthalocyanine), continue to be at the forefront of modern chemistry owing to their unique chemical[1,2] and physical properties[1,3] In particular, rare-earth phthalocyanines, i.e., $LnPc_2$ and Ln_2Pc_3 (Ln = lanthanide), have received considerable attention in the past few years due to their unique electrochromic,[1] spectral,[2] and conducting properties.[3]

Rare-earth phthalocyanines are attractive building blocks for molecule-based magnets due to the lanthanide, which may possess up to seven unpaired electrons (i.e., $S = {}^7/_2$). In their neutral form, $LnPc_2$ are characterized as having stable phthalocyaninate(2−) and radical phthalocyaninate(1−) ligands consisting of $(Pc^{2-})Ln^{+3}(Pc^{\bullet-})$ in resonance with $(Pc^{\bullet-})Ln^{3+}(Pc^{2-})$[4] or as $Ln^{4+}(Pc^{2-})_2$ for Ln = Ce.[5] Upon facile reduction to the monoanion the complex may be described as $[Ln^{3+}(Pc^{2-})_2]^-$, which in the case of $[LuPc_2]^-$ was confirmed by NMR.[2a] In contrast, oxidation to $[LnPc_2]^+$ leads to two possible electronic structures, i.e., $[Pc^{2-}Ln^{3+}Pc^0]^+$ {in resonance with $[Pc^0Ln^{3+}Pc^{2-}]^+$} or $[Pc^{\bullet-}Ln^{3+}Pc^{\bullet-}]^+$, as well as systems with tetravalent Ln (i.e., $Pc^{2-}Ln^{4+}Pc^{2-}$). Very few oxidized $LnPc_2$ species have been characterized; however, $[LuPc_2]^+[SbF_6]^-$ is reported to be diamagnetic;[4c] hence it must be described as $[Pc^{2-}Lu^{3+}Pc^0]^+$ or $[Lu^{3+}(Pc^{\bullet-})_2]^+$ with strong antiferromagnetic coupling between the $S = {}^1/_2$ $Pc^{\bullet-}$ units. For spin-containing lanthanide, e.g., Gd^{3+}, the $S = {}^7/_2$ Gd^{3+} and $S = {}^1/_2$ $Pc^{\bullet-}$ are strongly coupled for $GdPc_2$ leading to an $S = 3$ ground state.[4d] Furthermore, on the basis of the absence of an EPR signal assignable to $Pc^{\bullet-}$ and the presence of an EPR signal assignable to Gd^{3+}, the ground state was reported to have a $[Pc^0Gd^{3+}Pc^{2-}]^+$ electronic structure,[4b,c] which was modeled by MO calculations.[6]

$LnPc_2$ with the added feature of possessing spin-bearing ligands has a structural relationship to $S = {}^1/_2$ $[Fe^{III}(C_5Me_5)_2]^+$, a key component in the first organic magnet, $[Fe^{III}(C_5Me_5)_2]^+[TCNE]^{\bullet-}$ (TCNE = tetracyanoethylene) (T_c = 4.8 K).[7] Hence, $[GdPc_2]^+[TCNE]^{\bullet-}$ due to the presence of $g = 2$, $L = 0$ Gd^{3+}, was targeted for synthesis. Although TCNE was insufficient to oxidize $GdPc_2$, $C_4(CN)_6$[8] was reacted with $GdPc_2$ forming $[GdPc_2][C_4(CN)_6]$, **1**. In accord with previous work, $GdPc_2$ has several sites that can be oxidized, namely, $Pc^{\bullet-}$, and Pc^{2-}, and unlikely, but observed for other Ln^{3+}'s, Gd^{3+}. Hence, $[GdPc_2][C_4(CN)_6]$ is valence ambiguous as it may be formulated in many ways, e.g., (i) $[Gd^{3+}Pc_2]^0[C_4(CN)_6]^0$, (ii) $[Gd^{3+}(Pc^{\bullet-})_2]^+[C_4(CN)_6]^{\bullet-}$, (iii) $[Gd^{3+}(Pc^0)(Pc^{2-})]^+[C_4(CN)_6]^{\bullet-}$, or their resonance structures.[4d] Herein, we report the crystal and electronic structures of **1**.

$GdPc_2$[4c] and $C_4(CN)_6$[8] were prepared by literature methods. **1** was prepared from the reaction of $GdPc_2$ (24.7.0 mg, 0.0208 mmol) and $C_4(CN)_6$ (25.0 mg, 0.122 mmol) each dissolved in 20 mL of PhCl and stirred under nitrogen at room temperature for 4 h. The resulting dark green microcrystalline precipitate was then collected by vacuum filtration. Single crystals were grown in a 20 mL "H-tube" crystallization cell loaded with 7.1 mg of $C_4(CN)_6$ in 0.5 mL of CH_2Cl_2 and 10 mg of $GdPc_2$ mixed in 0.5 mL of CH_2Cl_2 in different ends of the tube. Chlorobenzene was added to the cell very slowly so as not to mix with the starting materials. The diffusion was completed in 3 weeks, and small crystals were observed on the wall of the flask: IR (Nujol, cm^{-1}) ν_{CN} 2185 (m), 2155 (m), 2071 (w).

The presence of isolated $[C_4(CN)_6]^{\bullet-}$ was confirmed by characteristic shifts in the ν_{CN} absorptions 2185, 2155, and 2071 cm^{-1},[9] while $[Gd^{3+}Pc_2]^+$ was confirmed by IR spectroscopy with a characteristic absorptions band at 1319 cm^{-1}. The latter absorption is lower than that of other cationic phthalocyanine radicals, e.g., $[Co^{II}Pc^{\bullet-}]^+$ (1358 cm^{-1}), $[Ni^{II}Pc^{\bullet-}]^+$ (1356 cm^{-1}), and $[H_2Pc^{\bullet}]^+$ (1365 cm^{-1}), but consistent with the neutral $Ln^{III}(Pc^{2-})(Pc^{\bullet-})$ radicals that range from 1315 to 1320 cm^{-1},[10] suggesting the presence of both Pc^{2-} and $Pc^{\bullet-}$.

The structure of $[GdPc_2][C_4(CN)_6]{\cdot}2PhCl$[11] consists of isolated $[GdPc_2]^+$, $[C_4(CN)_6]^{\bullet-}$, and two PhCl solvates, Figure 1. The Gd−N bond distances average 2.424 Å, and all the bond distances

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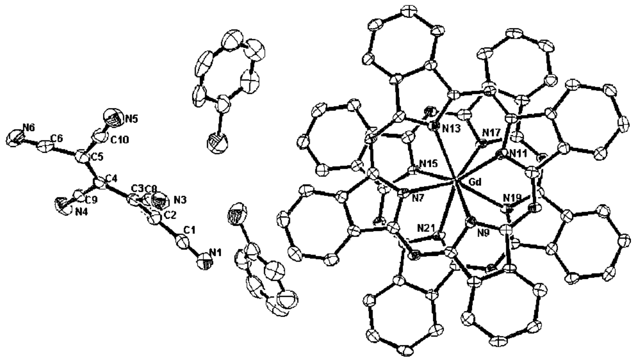

Figure 1. ORTEP drawing (50% probability ellipsoids) of $[\mathrm{GdPc_2}][\mathrm{C_4(CN)_6}]\cdot 2\mathrm{PhCl}$. Hydrogen atoms have been omitted for clarity.

and angles of $[\mathrm{GdPc_2}]^+$ are typical of other known $\mathrm{LnPc_2}$ complexes.[12] Gd^{3+} is eight coordinate and bonded to two phthalocyanines in a distorted square-antiprismatic coordination environment with two essentially planar and parallel Pc mean planes. The Pc−Pc intraplanar separation is 3.07 Å, which is close to that of the neutral $\mathrm{GdPc_2}$.[12] The staggering angle between the phthalocyanines is 46.7°, larger than that reported for $[(n\text{-Bu})_4\mathrm{N}][\mathrm{Gd^{III}(Pc^{2-})_2}]$ (34.5°),[12] but close to that for $\{[\mathrm{PPh_3}]_2\mathrm{N}\}[\mathrm{Gd^{3+}(Pc^{2-})_2}]$ (43.6°).[13]

The C−C bond distances for the $\mathrm{C_4}$ backbone of $\mathrm{C_4(CN)_6}$ range from 1.408(9) to 1.422(9) Å averaging 1.414(9) Å, in good agreement with predicted values for bond order of 1.5 expected for $[\mathrm{C_4(CN)_6}]^{\bullet-}$.[7] The average C−CN bond distances for the *exo*, *endo*, and *interior* positions are 1.419, 1.433, and 1.453 Å, respectively; hence they are chemically equivalent and average 1.435 Å. This average is slightly larger than that found for $[\mathrm{C_4(CN)_6}]^{2-}$ (1.427 Å), but significantly shorter than that observed for $\mathrm{C_4(CN)_6}^0$ (1.471 Å) consistent with the presence of $[\mathrm{C_4(CN)_6}]^{\bullet-}$.[7] The most surprising structural feature of the $[\mathrm{C_4(CN)_6}]^{\bullet-}$ is the pronounced torsion angle along the $\mathrm{C_4}$ backbone of 161.3°, close to that of the dimerized $[\mathrm{C_4(CN)_6}]^{\bullet-}$ (170.8°);[14] however, both are inconsistent with $\mathrm{C_4(CN)_6}^0$,[7] which has a twisted conformation, with a more pronounced 40° dihedral angle. Hence, to balance charge $[\mathrm{GdPc_2}]^+$ must be the counterion.

There are two distinct molecular stacking motifs known for $\mathrm{LnPc_2}$ species; either the $\mathrm{LnPc_2}$'s stack in pseudo-chains, e.g., $\mathrm{GdPc_2}$, or as isolated units, e.g., $[\mathrm{Ce(Pc)_2}][\mathrm{BF_4}]_{0.33}$.[5b] $[\mathrm{GdPc_2}][\mathrm{C_4(CN)_6}]\cdot 2\mathrm{PhCl}$ belongs to the former arrangement with stacks of $[\mathrm{GdPc_2}]^+$ along *a* with $[\mathrm{C_4(CN)_6}]^{\bullet-}$ and PhCl's filling channels. Along *a* the $[\mathrm{GdPc_2}]^+$ form a tilted array with a 14.2° tilt between $\mathrm{GdPc_2}$ moieties. Interestingly the $[\mathrm{GdPc_2}]^+$ stack such that the phthalocyanine of each $[\mathrm{GdPc_2}]^+$ is eclipsed with respect to the next $[\mathrm{GdPc_2}]^+$, with an inter-phthalocyanine distance of 3.612 Å. A similar arrangement was observed for α-$[\mathrm{LiPc}]^{\bullet-}$ that exhibits a tilt angle and inter-phthalocyanine spacing of 26.5° and 3.8 Å, respectively.[15] The twisted $[\mathrm{C_4(CN)_6}]^{\bullet-}$ and lack of the ···DADA··· $\{\mathrm{D} = [\mathrm{GdPc_2}]^+, \mathrm{A} = [\mathrm{C_4(CN)_6}]^{\bullet-}\}$ alternating chain structure as observed for other classes of molecule-based magnets[16] suggest that this material stabilizes magnetic ordering.

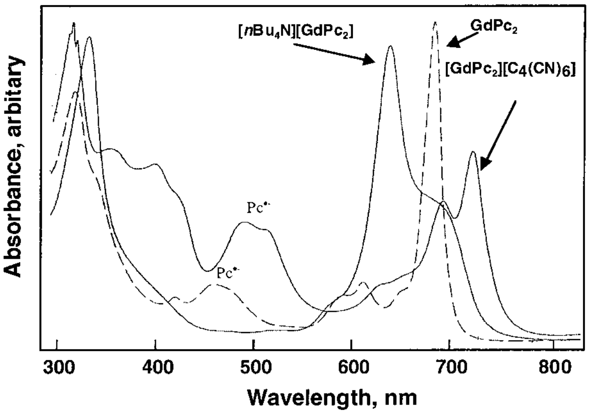

Figure 2. UV−vis spectra of $\mathrm{GdPc_2}$, $[\mathrm{GdPc_2}]^+[\mathrm{C_4(CN)_6}]^-$, and $[n\text{-Bu}_4\mathrm{N}]^+[\mathrm{GdPc_2}]^-$.

The electronic spectrum of $[\mathrm{GdPc_2}][\mathrm{C_4(CN)_6}]$ in $\mathrm{CH_2Cl_2}$ exhibits absorptions at 318, 357, 400, 489, 518 sh, 622 sh, 682, and 709 nm (Figure 2), where the 318 nm band is assigned to the B-band (MLCT) absorption, and the 489 and 518 nm bands are assigned to the presence of $\mathrm{Pc}^{\bullet-}$ $[2\mathrm{e_g}\ (\pi) \rightarrow 2\mathrm{a_{1u}}\ (\pi)]$, while the 682 and 709 nm bands are assigned to Q-bands $[\mathrm{a_{1u}}\ (\pi) \rightarrow \mathrm{e_g}\ (\pi^*)]$.[17] The remaining bands are attributed to $[\mathrm{C_4(CN)_6}]^{\bullet-}$ absorptions.[7,10] These assigned bands represent shifts with respect to absorptions for $\mathrm{Gd^{3+}Pc_2}$ of 322, 460, 472 sh, 604, and 671 nm.[17] As with $\mathrm{Gd^{3+}Pc_2}$, which exhibits an absorption at 458 and shoulder at 472 nm attributed to $\mathrm{Pc}^{\bullet-}$, $[\mathrm{GdPc_2}]^+$ exhibits a broad absorption at 489 and shoulder at 518 nm consistent with the presence of $\mathrm{Pc}^{\bullet-}$. Reduction of $\mathrm{GdPc_2}$ to $[\mathrm{GdPc_2}]^-$ is accompanied by the disappearance of the characteristic $\mathrm{Pc}^{\bullet-}$ absorption at 460 nm, consistent with the $[\mathrm{Pc^{2-}Gd^{3+}Pc^{2-}}]^-$ representation.[17] Hence, oxidation of $\mathrm{Gd^{3+}Pc_2}$ to the cation, $[\mathrm{GdPc_2}]^+$, leads to a shift in the $\mathrm{Pc}^{\bullet-}$ absorption to 489 nm consistent with the formulation of **1** as $[\mathrm{Gd^{3+}(Pc^{\bullet-})_2}][\mathrm{C_4(CN)_6}]^{\bullet-}$, with four paramagnetic centers. Insufficient material hampered the detailed study of the magnetic behavior of **1**; however, preliminary studies did not show evidence for magnetic ordering.

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(11) Crystal data: triclinic space group $P\bar{1}$ (No. 2), $a = 13.2324(2)$ Å, $b = 15.6369(3)$ Å, $c = 18.2546(3)$ Å, $\alpha = 110.770(8)°$, $\beta = 97.788(1)°$, $\gamma = 97.772(9)°$, $Z = 2$. Cell constants and orientation matrix were obtained from 10 images exposed for 30 s at 200 K on a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and expanded using Fourier techniques using the SIR92[18a] software package. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included, but not refined, using SHELX97-2[18b] as part of the WinGX[18c] graphics suite. The final cycle of full-matrix least-squares refinement was based on 4563 observed reflections $[I_o > 2.00\sigma(I)]$ and 366 variable parameters and converged with unweighted and weighted agreement factors $R = 0.0285$ and $R_w = 0.0882$, respectively.

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