

Figure 4. Structure of $\text{Ca}_2\text{V}(\text{PO}_4)(\text{P}_2\text{O}_7)$ showing the coordination of PO_4 and P_2O_7 ligands around VO_6 octahedra. Thermal ellipsoids are shown at the 60% probability level.

Connection between adjacent layers is provided by O—Ca—O bonds, as shown by the dashed lines in Figure 2. The water molecules are also coordinated to the Ca atoms. Thus, in the TG analysis the release of one lattice water molecule, which occurs at rather high temperature, is not resolved from the second step corresponding to the condensation of two HPO_4 groups to a P_2O_7 group. The coordination number (CN) of Ca is assigned on the basis of two criteria: the maximum gap in the Ca—O distances and the bond valence sums for Ca. Therefore, the Ca atom is coordinated by nine oxygen atoms with an average Ca—O distance of 2.575 Å.

$\text{Ca}_2\text{V}(\text{PO}_4)(\text{P}_2\text{O}_7)$. The structure of this compound, viewed along the a and b axes, is shown in Figure 3. It contains intersecting channels where the Ca^{2+} cations are located. The framework consists of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. The conversion of $\text{Ca}_2\text{V}(\text{PO}_4)(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ to $\text{Ca}_2\text{V}(\text{PO}_4)(\text{P}_2\text{O}_7)$ is difficult to explain mechanis-

tically. To our knowledge, $\text{Ca}_2\text{V}(\text{PO}_4)(\text{P}_2\text{O}_7)$ is the first vanadium phosphate containing both PO_4 and P_2O_7 groups in the structure. As shown in Figure 4, each VO_6 octahedron shares its corners with two PO_4 and three P_2O_7 groups. One of the diphosphate groups is coordinated to the V atom as a bidentate ligand. The VO_6 octahedron in the dehydrated compound is more distorted than that in the hydrate as shown by the V—O bond lengths. Each phosphate group shares two corners with two VO_6 octahedra, with the remaining two oxygen atoms being bonded to the Ca atoms. Each diphosphate group is bonded to a V atom as a chelate and bonded to two V atoms as a monodentate ligand. The remaining two oxygen atoms of the diphosphate group are bonded to the Ca atoms only. The PO_4 tetrahedra of a P_2O_7 group are in a semi-eclipsed configuration. The P atoms are displaced away from the bridging oxygen atoms, O(7), so that one longer and three shorter P—O bonds are formed. The P(1)—O(7)—P(2) bond angle is $130.8(2)^\circ$. Atoms Ca(1) and Ca(2) occupy sites within the channels and are eight- and nine-coordinated, with average Ca—O distances of 2.572 and 2.577 Å, respectively. The connectivity formula can be represented as ${}^3_0\text{Ca}_2[\text{V}(\text{PO}_4)_{2/2}(\text{P}_2\text{O}_7)_{1/3}(\text{P}_2\text{O}_7)_{2/3}]$.

Hydrothermal techniques are useful for the synthesis of new phases in the form of single crystals suitable for structure analysis. $\text{Ca}_2\text{V}(\text{PO}_4)(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, which contains hydrogen phosphate groups and a water of hydration, was synthesized under mild conditions. Interestingly, crystals of the dehydrated compound, $\text{Ca}_2\text{V}(\text{PO}_4)(\text{P}_2\text{O}_7)$, were obtained under much more vigorous conditions. This research shows that the use of different PT conditions can aid the search for new crystalline phases.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond angles (5 pages); tables of observed and calculated structure factors for both compounds (13 pages). Ordering information is given on any current masthead page.

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1,4-Phenylene-Bridged 1,3,2,4,6-Thia- and 1,3,2,4,6-Selenaphosphatriazinyl Diradicals: Preparation, Spin Distributions, and Solid-State Structures

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The 1,4-phenylene-bridged bis(1,3,2,4,6-thiaphosphatriazine) and bis(1,3,2,4,6-selenaphosphatriazine) compounds ($\text{ClEN}_3\text{PPh}_2\text{C}_6\text{H}_4(\text{CPPh}_2\text{N}_3\text{ECl})$ ($\text{E} = \text{S}, \text{Se}$) have been prepared by the reactions of 1,4-phenylenebis(phosphimidoylamidine), $(\text{Me}_3\text{Si})_2\text{NPPh}_2(\text{Me}_3\text{SiN})\text{CC}_6\text{H}_4\text{C}(\text{NSiMe}_3)\text{PPh}_2\text{N}(\text{SiMe}_3)_2$, with SCl_4 and SeCl_4 . Reduction of these E -chloro derivatives with triphenylantimony affords the corresponding bis(thiaphosphatriazinyl) and bis(selenaphosphatriazinyl) diradicals, $(\text{EN}_3\text{PPh}_2\text{C}_6\text{H}_4(\text{CPPh}_2\text{N}_3\text{E}))$ ($\text{E} = \text{S}, \text{Se}$). The ESR spectra of these materials in CH_2Cl_2 are consistent with noninteracting radicals, an observation suggested to arise from association of radicals through a single terminus. The solid-state structure of the selenium compound, $(\text{SeN}_3\text{PPh}_2\text{C}_6\text{H}_4(\text{CPPh}_2\text{N}_3\text{Se}))$, reveals association through both termini to produce a centrosymmetric dimer. Association occurs through Se—N rather than Se—Se linkages. Crystals of $\text{C}_{32}\text{H}_{24}\text{N}_6\text{P}_2\text{Se}_2 \cdot 2\text{CH}_3\text{CN}$ belong to the rhombohedral space group $R\bar{3}$; $fw = 794.6$, $a = 34.431(12)$ Å, $c = 17.513(4)$ Å, and $Z = 9$.

Introduction

There is growing interest in the study of heterocyclic thiazyl and selenazyl radicals, in particular the factors that control the nature and strength of their association, both in solution and in the solid state.¹ Such interactions are known to provide pathways for structural change^{2,3} and, in suitably designed cases, provide

solid-state structures with interesting electrical and magnetic properties.^{4,5} Within the context of both these issues, we recently

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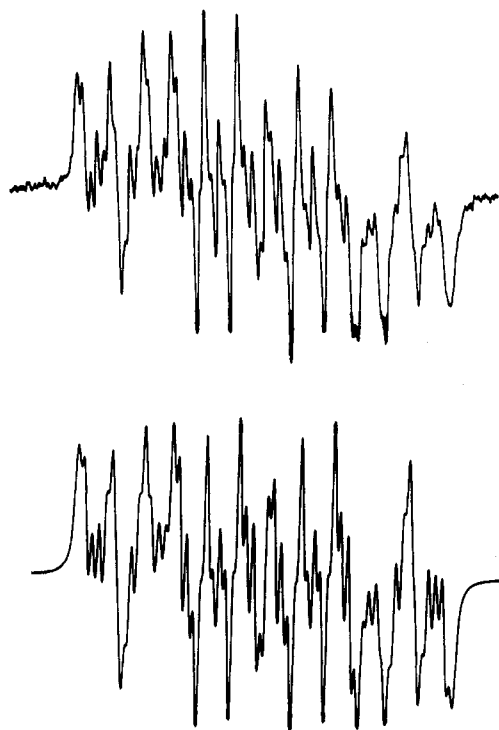
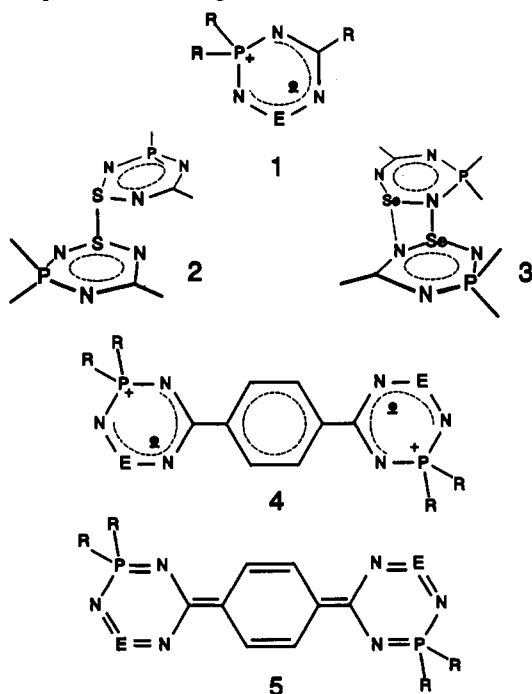


Figure 1. ESR spectrum of 4 (E = S) in CH_2Cl_2 (above) and computer simulation (below). Coupling constants used in the simulation are given in Table I. Line broadening was set at 0.04 mT.

reported the preparation and ESR and structural (X-ray) characterization of the 1,3,2,4,6-thia- and 1,3,2,4,6-selenaphosphotriazinyl radicals $[\text{R}_2\text{P}(\text{RC})\text{N}_3\text{E}]^\bullet$ (E = S, Se) (1).⁶ Despite remarkably similar spin distributions, the two radicals associate in the solid state in very different fashions. The former (E = S) dimerizes via a S---S linkage, i.e., 2; the latter, via an Se---N bond, to produce the charge transfer adduct 3.



Scheme I

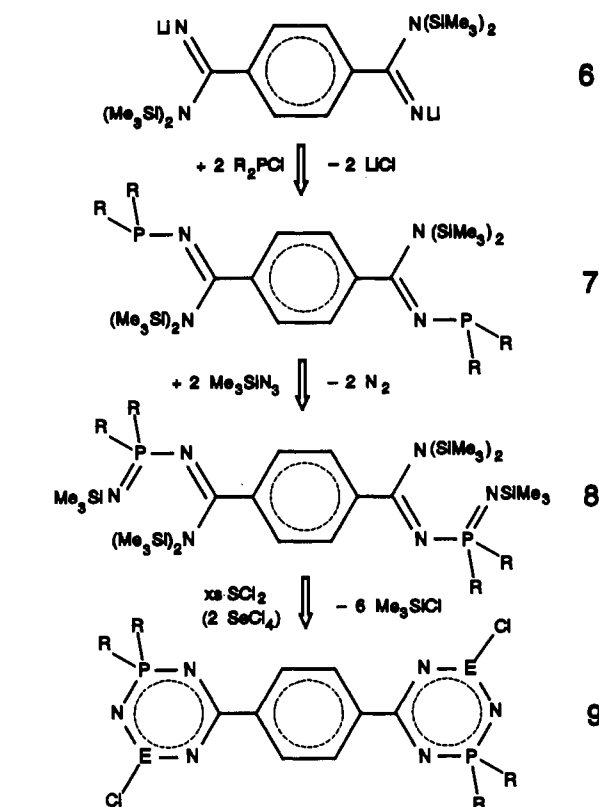


Table I. Hyperfine Coupling Constants (mT) and g Values for 1 and 4 (R = Ph)

	E	g	$a(\text{N}2)$	$a(\text{N}4)$	$a(\text{N}6)$	$a(\text{P})$
1 ^a	S	2.0057	0.555	0.111	0.187	0.420
4 ^b	S	2.0056	0.576	0.086	0.199	0.458
1	Se	2.0171	0.630	0.141	0.186	0.544
4	Se	2.0170	0.635	0.141	0.186	0.535

^a Coupling to three protons with $a(\text{H}) = 0.035$ mT also observed.

^b Coupling to two protons with $a(\text{H}) = 0.038$ mT also observed.

terparts, i.e., 4, our intent being to examine the mode of association of these derivatives and also the extent of spin coupling between the two radical centers. It was not clear to us, for example, whether the electronic structure would be truly diradical in nature, i.e., 4, or whether a closed-shell quinoidal ground state, 5, would prevail.

Results and Discussion

Preparation of 4 (E = S, Se). The preparation of monocyclic derivatives based on the six-membered heterocyclic PCN_3E framework involved the condensation of a phosphimidoylamidine with sulfur or selenium halides.⁶ Extension of this method (Scheme I) affords the bifunctional materials reported here. Thus, the reaction of the bis(*N*-lithioamidine) 6 with Ph_2PCl provides a high-yield route to the bis(phosphine) 7.⁷ The latter compound can then be oxidized with trimethylsilyl azide to the corresponding bis(phosphimidoylamidine) 8. Finally, condensation of 7 with either SCl_2 or SeCl_4 provides the bifunctional *S*- (or *Se*-) chloro heterocyclic derivatives 9. Reduction of these materials to the diradicals 4 can be effected with triphenylantimony.

ESR Spectra. ESR spectra (Figures 1 and 2) of 4 were recorded at ambient temperature on samples dissolved in dichloromethane. Hyperfine coupling constants a_{P} , a_{N} , and a_{H} (Table I) were extracted by full spectral simulation⁸ (simulated spectra are shown

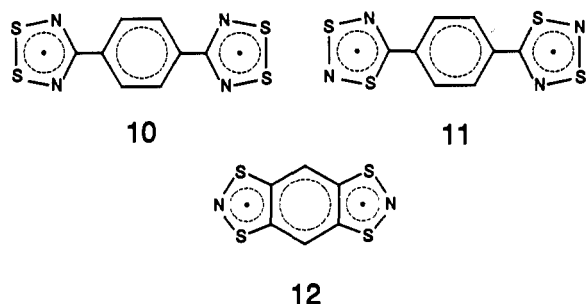
In the present paper, we extend the study of these monofunctional radicals to their bifunctional 1,4-phenylene-bridged coun-

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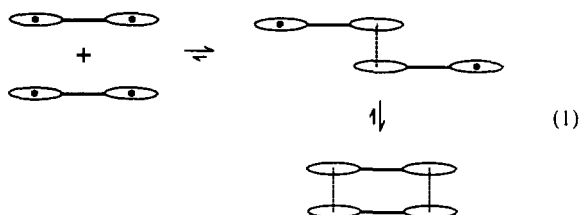
- (7) A similar reaction, that of 6 with (diisopropylamino)dichlorophosphine, has recently been reported: Roques, C.; Mazières, M.-R.; Majoral, J.-P.; Sanchez, M. *Inorg. Chem.* **1989**, *28*, 1328.
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in Figure 1). Comparison of the coupling constants of the bifunctional materials **4** with those of the corresponding monocyclic derivatives **1** reveals remarkably similar spin distributions in the two sets of compounds. The extent of spin leakage to the phenylene ortho protons ($a_H = 0.038$ mT) is also almost identical to that found in the monofunctional compounds. While some extra line-broadening in the high-field region is apparent in the spectra of **4**, the spectra show no significant indications of exchange coupling between two radical centers.

The absence of exchange interactions is at first surprising. In the bifunctional radical **10** such effects are certainly apparent, in spite of the fact that the symmetry of the SOMO, which prohibits, at least to first order, through-bond interactions between the radical ring and phenylene group. The absence of exchange



has, however, been observed in the diradicals **11** and **12**.^{9,10} In the case of **12** it has been suggested that radical association may be the important. Accordingly if two diradicals were to associate through only one terminus (eq 1), the remaining two radical sites



would be sufficiently removed from one another to render through-space interactions almost negligible. A similar effect, i.e., association into open-chain oligomers, has been proposed to account for the ESR spectra of thioaminy diradicals¹¹ and may well be operative here. Although we have no quantitative ESR measurements, the signal intensities arising from solutions of **4** (E = S, Se) are significantly weaker than those of, for example, simple thia- and selenatriazinyls [$\text{Ph}_2\text{C}_2\text{N}_3\text{E}$]^{*}, where the degree of association has been quantified.¹²

The ³¹P NMR spectra of solutions of **4** (E = S, Se) in CDCl_3 consist of clear, sharp singlets. When considered together with the qualitative observation that the ESR signal intensity of **4** (E = S, Se) is relatively weak, the NMR evidence suggests that the dominant species in solution is diamagnetic. In view of the solid-state structure of **4** (E = Se) described below, the appearance of a single resonance in the ³¹P NMR spectrum indicates either that the modes of association in solution and the solid state are not the same or that exchange between associated and dissociated materials is fast on the NMR time scale.

Solid-State Structure of 4 (E = Se). Crystals of **4** (either S or Se) suitable for X-ray analysis were difficult to obtain. The sulfur compound precipitated as an amorphous glass from a variety of solvents, and although good-quality crystals of the selenium compound could be grown from $\text{CHCl}_3/\text{CH}_3\text{CN}$, they readily degraded as a result of loss of occluded solvent. Eventually, however, we were able to mount crystals of **4** (E = Se) in sealed

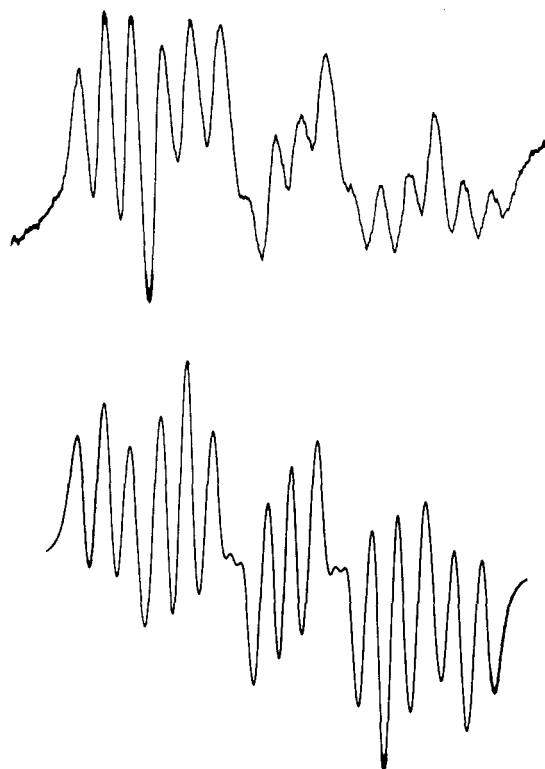


Figure 2. ESR spectrum of **4** (E = Se) in CH_2Cl_2 (above) and computer simulation (below). Coupling constants used in the simulation are given in Table I. Line broadening was set at 0.10 mT.

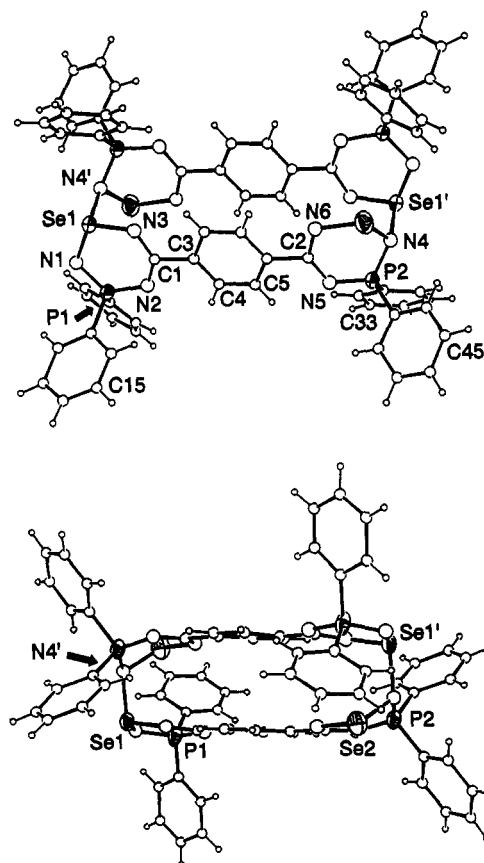


Figure 3. ORTEP drawings of the dimer of **4** (E = Se), showing (above) the atom-numbering scheme and (below) the ring conformations. Note that in these drawings the C atoms have been assigned arbitrary thermal factors.

tubes in the presence of solvent, and a reasonable data set, sufficient certainly for basic structural elucidation, was obtained. As

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Table II. Positional Parameters for the Dimer of 4 (E = Se)^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} , Å ²
Se(1)	0.00512 (8)	0.26175 (8)	0.03526 (14)	3.2 (2)
Se(2)	-0.32080 (8)	0.16227 (9)	0.20687 (16)	4.5 (2)
P(1)	0.0322 (2)	0.2890 (2)	0.1890 (4)	3.6 (4)
P(2)	-0.2877 (2)	0.1697 (2)	0.3566 (4)	3.0 (4)
N(1)	0.0479 (6)	0.2865 (6)	0.1039 (11)	3.9 (4)
N(2)	-0.0208 (6)	0.2677 (6)	0.2039 (10)	3.5 (4)
N(3)	-0.0470 (5)	0.2510 (5)	0.0726 (10)	3.1 (4)
N(4)	-0.3284 (5)	0.1329 (5)	0.3038 (9)	2.9 (4)
N(5)	-0.2410 (5)	0.1971 (5)	0.3175 (10)	2.8 (4)
N(6)	-0.2611 (6)	0.1844 (6)	0.1863 (10)	3.3 (4)
C(1)	-0.0503 (7)	0.2554 (7)	0.1482 (13)	2.4 (5)
C(2)	-0.2339 (7)	0.1974 (7)	0.2449 (13)	3.1 (5)
C(3)	-0.0976 (7)	0.2393 (7)	0.1749 (13)	2.5 (5)
C(4)	-0.1088 (7)	0.2394 (7)	0.2495 (12)	2.8 (5)
C(5)	-0.1523 (7)	0.2265 (6)	0.2720 (11)	2.2 (5)
C(6)	-0.1855 (6)	0.2138 (6)	0.2187 (11)	1.7 (4)
C(7)	-0.1745 (7)	0.2152 (7)	0.1420 (12)	2.9 (5)
C(8)	-0.1313 (7)	0.2278 (7)	0.1182 (13)	3.5 (5)
C(11)	0.0572 (8)	0.3454 (7)	0.2126 (12)	3.3 (5)
C(12)	0.1028 (10)	0.3724 (10)	0.2088 (16)	6.5 (7)
C(13)	0.1248 (9)	0.4205 (9)	0.2273 (15)	5.7 (7)
C(14)	0.0990 (9)	0.4376 (8)	0.2456 (15)	5.1 (6)
C(15)	0.0546 (9)	0.4119 (9)	0.2526 (15)	5.6 (7)
C(16)	0.0321 (9)	0.3665 (10)	0.2338 (16)	5.9 (7)
C(21)	0.0560 (8)	0.2685 (7)	0.2560 (14)	3.8 (6)
C(22)	0.0872 (10)	0.2575 (10)	0.2312 (17)	7.5 (8)
C(23)	0.1077 (12)	0.2401 (13)	0.2854 (25)	11.1 (11)
C(24)	0.0957 (12)	0.2369 (12)	0.3613 (22)	9.8 (10)
C(25)	0.0634 (11)	0.2477 (10)	0.3831 (18)	8.0 (9)
C(26)	0.0429 (9)	0.2624 (8)	0.3286 (16)	5.3 (7)
C(31)	-0.2810 (7)	0.1425 (7)	0.4342 (12)	2.5 (5)
C(32)	-0.2421 (8)	0.1433 (7)	0.4513 (13)	4.0 (6)
C(33)	-0.2388 (9)	0.1213 (9)	0.5155 (16)	5.4 (7)
C(34)	-0.2747 (10)	0.0965 (9)	0.5628 (16)	6.2 (7)
C(35)	-0.3130 (10)	0.0932 (9)	0.5468 (16)	6.4 (7)
C(36)	-0.3181 (8)	0.1163 (8)	0.4847 (14)	4.3 (6)
C(41)	-0.3056 (7)	0.2052 (7)	0.3947 (12)	2.7 (5)
C(42)	-0.2753 (8)	0.2443 (9)	0.4252 (14)	4.9 (6)
C(43)	-0.2897 (11)	0.2723 (10)	0.4570 (18)	8.3 (9)
C(44)	-0.3327 (10)	0.2632 (10)	0.4550 (16)	6.6 (7)
C(45)	-0.3631 (10)	0.2234 (11)	0.4212 (17)	7.5 (8)
C(46)	-0.3483 (8)	0.1952 (8)	0.3921 (13)	4.2 (6)
C(S1)	0.17392	0.23883	0.64685	10.8 (11)
C(S2)	0.14028	0.25255	0.60834	14.2 (14)
N(S1)	0.12581	0.26988	0.57852	24.5 (20)
C(S3) ^b	0.83978	0.87475	0.72231	9.7 (13)
C(S4) ^b	0.88016	0.98394	0.71293	8.2 (19)
C(S5) ^b	0.86250	0.93750	0.72658	10.3 (27)
C(S6) ^b	0.87139	0.86908	0.66651	11.6 (25)

^aC(S1)–C(S6) and N(S1) are the atoms of disordered solvent molecules located from Fourier and difference maps. These were included in the final stages of least-squares refinement. Only the isotropic thermal parameters of these seven atoms were allowed to vary. The site occupancy factors are 1.0 unless otherwise specified. *B*_{iso} is the mean of the principal axes of the thermal ellipsoid. ^bOccupancies: C(S3), 0.75; C(S4), 0.47; C(S5), 0.39; C(S6), 0.46.

grown from CH₃CN/CHCl₃, crystals of 4 (E = Se) belong to the rhombohedral space group *R* $\bar{3}$. The structure consists of discrete dimers linked through two Se–N bonds (as in the case of 3). Figure 3 illustrates two ORTEP drawings of the dimer, one showing the atom-numbering scheme and the other showing the exactly parallel alignment of the two phenylene bridges (as required by symmetry) and the puckering of the N-bonded heterocycles. Table II provides a listing of non-hydrogen atom coordinates, and Table III summarizes bond length and angle information.

The halves of the dimer are related by an inversion center. As observed in the dimer 3 of the monofunctional radical 1 (E = Se), association occurs in the rather unusual charge-transfer mode, to produce linked rings which can be formally regarded as cation–anion pairs. Certainly the bond length variations in the Se- and N-bonded rings (see Table III) are consistent with the differences expected upon oxidation or reduction of the neutral radical which, on the basis of RHF MNDO calculations on model structures, has a SOMO distribution 13.⁶ Alternatively, within

Table III. Bond Lengths (Å) and Bond Angles (deg) in the Dimer of 4 (E = Se)^a

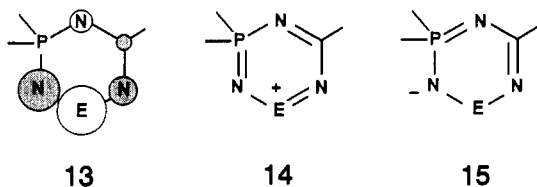
Bond Lengths			
Se(1)–N(1)	1.756 (18)	C(11)–C(12)	1.37 (4)
Se(1)–N(3)	1.766 (17)	C(11)–C(16)	1.43 (4)
Se(1)–N(4)'	1.963 (16)	C(12)–C(13)	1.47 (4)
Se(2)–N(4)	1.927 (17)	C(13)–C(14)	1.32 (4)
Se(2)–N(6)	1.834 (17)	C(14)–C(15)	1.34 (4)
P(1)–N(1)	1.60 (2)	C(15)–C(16)	1.40 (4)
P(1)–N(2)	1.61 (2)	C(21)–C(22)	1.37 (4)
P(1)–C(11)	1.73 (2)	C(21)–C(26)	1.33 (4)
P(1)–C(21)	1.77 (2)	C(22)–C(23)	1.48 (5)
P(2)–N(4)	1.63 (2)	C(23)–C(24)	1.38 (6)
P(2)–N(5)	1.56 (2)	C(24)–C(25)	1.39 (5)
P(2)–C(31)	1.73 (2)	C(25)–C(26)	1.42 (4)
P(2)–C(41)	1.75 (2)	C(31)–C(32)	1.36 (3)
N(2)–C(1)	1.32 (3)	C(31)–C(36)	1.44 (3)
N(3)–C(1)	1.34 (3)	C(32)–C(33)	1.39 (4)
N(5)–C(2)	1.29 (3)	C(33)–C(34)	1.37 (4)
N(6)–C(2)	1.31 (3)	C(34)–C(35)	1.30 (4)
C(1)–C(3)	1.51 (3)	C(35)–C(36)	1.41 (4)
C(2)–C(6)	1.54 (3)	C(41)–C(42)	1.33 (3)
C(3)–C(4)	1.36 (3)	C(41)–C(46)	1.33 (3)
C(3)–C(8)	1.42 (3)	C(42)–C(43)	1.40 (4)
C(4)–C(5)	1.39 (3)	C(43)–C(44)	1.35 (5)
C(5)–C(6)	1.37 (3)	C(44)–C(45)	1.38 (4)
C(6)–C(7)	1.39 (3)	C(45)–C(46)	1.40 (4)
C(7)–C(8)	1.39 (3)		
Bond Angles			
N(1)–Se(1)–N(3)	111.4 (8)	C(2)–C(6)–C(7)	122 (2)
N(1)–Se(1)–N(4)'	102.2 (7)	C(5)–C(6)–C(7)	118 (2)
N(3)–Se(1)–N(4)'	100.4 (7)	C(6)–C(7)–C(8)	122 (2)
N(4)–Se(2)–N(6)	102.8 (7)	C(3)–C(8)–C(7)	118 (2)
N(1)–P(1)–N(2)	117 (1)	P(1)–C(11)–C(12)	121 (2)
N(1)–P(1)–C(11)	107 (1)	P(1)–C(11)–C(16)	123 (2)
N(1)–P(1)–C(21)	111 (1)	C(12)–C(11)–C(16)	116 (2)
N(2)–P(1)–C(11)	107 (1)	C(11)–C(12)–C(13)	122 (2)
N(2)–P(1)–C(21)	111 (1)	C(12)–C(13)–C(14)	118 (2)
C(11)–P(1)–C(21)	103 (1)	C(13)–C(14)–C(15)	121 (2)
N(4)–P(2)–N(5)	117 (1)	C(14)–C(15)–C(16)	122 (2)
N(4)–P(2)–C(31)	109 (1)	C(11)–C(16)–C(15)	120 (2)
N(4)–P(2)–C(41)	107 (1)	P(1)–C(21)–C(22)	119 (2)
N(5)–P(2)–C(31)	107 (1)	P(1)–C(21)–C(26)	121 (2)
N(5)–P(2)–C(41)	111 (1)	C(22)–C(21)–C(26)	120 (2)
C(31)–P(2)–C(41)	106 (1)	C(21)–C(22)–C(23)	120 (3)
Se(1)–N(1)–P(1)	116 (1)	C(22)–C(23)–C(24)	117 (3)
P(1)–N(2)–C(1)	123 (1)	C(23)–C(24)–C(25)	119 (3)
Se(1)–N(3)–C(1)	118 (1)	C(24)–C(25)–C(26)	121 (3)
Se(1)–N(4)–Se(2)	115 (1)	C(21)–C(26)–C(25)	120 (2)
Se(1)–N(4)–P(2)	119 (1)	P(2)–C(31)–C(32)	124 (2)
Se(2)–N(4)–P(2)	105 (1)	P(2)–C(31)–C(36)	120 (2)
P(2)–N(5)–C(2)	125 (2)	C(32)–C(31)–C(36)	116 (2)
Se(2)–N(6)–C(2)	117 (1)	C(31)–C(32)–C(33)	121 (2)
N(2)–C(1)–N(3)	132 (2)	C(32)–C(33)–C(34)	122 (2)
N(2)–C(1)–C(3)	114 (2)	C(33)–C(34)–C(35)	119 (3)
N(3)–C(1)–C(3)	114 (2)	C(34)–C(35)–C(36)	121 (3)
N(5)–C(2)–N(6)	132 (2)	C(31)–C(36)–C(35)	120 (2)
N(5)–C(2)–C(6)	117 (2)	P(2)–C(41)–C(42)	120 (2)
N(6)–C(2)–C(6)	111 (2)	P(2)–C(41)–C(46)	122 (2)
C(1)–C(3)–C(4)	123 (2)	C(42)–C(41)–C(46)	119 (2)
C(1)–C(3)–C(8)	118 (2)	C(41)–C(42)–C(43)	119 (2)
C(4)–C(3)–C(8)	119 (2)	C(42)–C(43)–C(44)	123 (3)
C(3)–C(4)–C(5)	122 (2)	C(43)–C(44)–C(45)	116 (3)
C(4)–C(5)–C(6)	120 (2)	C(44)–C(45)–C(46)	119 (3)
C(2)–C(6)–C(5)	120 (2)	C(41)–C(46)–C(45)	123 (2)

^aSe(1)' and N(4)' are the symmetry equivalents of Se(1) and N(4). The prime refers to the following equivalent position: $-1/3 - x, 1/3 - y, 1/3 - z$.

a valence-bond context, the electronic structures of the two rings can be visualized in terms of the resonance structures 14 and 15. The internal consistency between the C–C bonds within the bridging phenylene group indicates little if any quinoidal contribution to the ground-state structure.

Summary

1,4-Phenylene-bridged thia- and selenaphosphatriaziny diradicals 4 can be generated by double reduction of the corre-



sponding chloro derivatives. ESR and NMR evidence suggests a pronounced association of these radicals in solution. The only ESR-observable species is suggested to be a partially associated open-chain dimer (or oligomer). In the solid state 4 (E = Se) associates through two Se-N bonds into a diamagnetic charge-transfer adduct. There is no evidence for any quinoidal interaction between the two heterocyclic rings.

Experimental Section

Starting Materials and General Procedures. 1,4-Dicyanobenzene (Aldrich), chlorodiphenylphosphine (Aldrich), trimethylsilyl azide (Aldrich), selenium powder (Alfa), and chlorine gas (Matheson) were all commercial products and were used as received. Sulfur dichloride (Aldrich) was freshly distilled before use. Triphenylantimony (Aldrich) was recrystallized from 2-propanol. Solvents were dried [diethyl ether (Fisher)/CaH₂, toluene (Fisher)/Na, acetonitrile (Fisher HPLC grade)/P₂O₅, hexane (Caledon)/CaH₂, methylene chloride (Fisher)/P₂O₅, chloroform (Fisher)/P₂O₅] and freshly distilled before use. All reactions were performed under an atmosphere of nitrogen (99.98% purity) unless otherwise specified. LiN(SiMe₃)₂Et₂O¹³ and SeCl₄¹⁴ were prepared by literature methods. Infrared spectra (2000–250 cm⁻¹) were recorded as Nujol mulls (CsI windows) on a Nicolet 20SX/C FTIR spectrometer. Melting points were obtained on an electrothermal melting point apparatus and were uncorrected. ³¹P NMR spectra were recorded (in CDCl₃, reference H₃PO₄, unless otherwise specified) on a Bruker WH-400 spectrometer. Chemical analyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of 7 (R = Ph). 1,4-Dicyanobenzene (16.0 g, 0.12 mol) and LiN(SiMe₃)₂Et₂O (60.0 g, 0.24 mol) were slurred together in 500 mL of diethyl ether. After 24 h, the ether was removed by distillation and replaced with toluene (250 mL). Chlorodiphenylphosphine (44.7 mL, 0.24 mol) in toluene (100 mL) was then added dropwise to the reaction flask, and the resulting mixture was refluxed overnight. The heavy precipitate of LiCl was removed by hot filtration, and the solution was concentrated by distillation to about 200 mL. Upon cooling of the solution to room temperature, bright yellow crystals of 7 (R = Ph) [43.5 g, 42.8%; mp 199–201 °C dec; δ(P) 36.4 (in toluene)] were obtained. IR (cm⁻¹): 1561 (s), 1497 (w), 1462 (s), 1377 (s), 1294 (m), 1244 (m), 1133 (s), 976 (s), 885 (s), 844 (s), 812 (w), 740 (m), 698 (s), 674 (w), 519 (s), 483 (m). Anal. Calcd for C₄₄H₆₀N₄P₂Si₄: C, 64.51; H, 7.38; N, 6.84. Found: C, 64.67; H, 7.51; N, 6.92.

Preparation of 8 (R = Ph). An excess of Me₃SiN₃ (5.0 mL, 37.4 mmol) was added to a solution of 7 (R = Ph) (10.0 g, 12.2 mmol) in 25 mL of toluene, and the mixture was stirred and heated at reflux for 18 h. The solvent was removed in vacuo to afford a yellow-orange oil. Acetonitrile (20 mL) was then added, which converted the oil to a pale yellow solid. Subsequent filtration of this solid and recrystallization from hexane (150 mL) afforded almost colorless blocks of 8 (R = Ph) [7.4 g, 61.1%; mp 174–176 °C; δ(P) -4.9]. IR (cm⁻¹): 1560 (s), 1500 (w), 1462 (s), 1436 (m), 1403 (w), 1377 (m), 1281 (s), 1256 (s), 1157 (m), 1108 (m), 1029 (w), 984 (m), 855 (s), 831 (s), 801 (s), 747 (m), 717 (m), 695 (s), 630 (w), 599 (w), 567 (w), 533 (s), 510 (w), 403 (w), 302 (w). Anal. Calcd for C₃₀H₁₈N₆P₂Si₆: C, 60.44; H, 7.91; N, 8.46. Found: C, 60.56; H, 7.70; N, 8.34.

Preparation of 9 (R = Ph, E = S). An excess of sulfur dichloride (0.5 g, 4.8 mmol) in 5 mL of CH₃CN was added dropwise to a stirred and hot solution of 8 (R = Ph) (1.0 g, 1.0 mmol) in 20 mL of CH₃CN. During the addition, the reaction mixture changed color from purple-red to bright yellow. Once a persistent yellow color was formed, the addition was halted and the solution then filtered. Subsequent cooling of the filtrate afforded bright yellow blocks of 9 (R = Ph, E = S) (0.5 g, 72.5%), which were recrystallized from CH₃CN [mp 250–252 °C dec; δ(P) 12.1]. IR (cm⁻¹): 1466 (s), 1438 (s), 1405 (m), 1377 (s), 1295 (s), 1270 (m), 1178 (s), 1126 (s), 1116 (s), 1089 (w), 1030 (s), 1029 (s), 1009 (s), 998 (m), 932 (m), 883 (w), 842 (w), 817 (m), 767 (m), 743 (m), 729

Table IV. Summary of Data Collection, Structure Solution, and Refinement Details

formula	C ₃₂ H ₂₄ N ₆ P ₂ Se ₂ ·2CH ₃ CN
fw	794.6
cryst size, mm	0.65 × 0.65 × 0.35
cryst syst	rhombohedral
a, Å	34.431 (12)
c, Å	17.513 (4)
V, Å ³	17980 (7)
space group	R3, No. 148
Z	9
F(000)	7200
d _{calcd} , g cm ⁻³	1.32
μ, mm ⁻¹	1.94
min/max abs cor	0.86/1.17
diffractometer	Enraf Nonius, CAD4
radiation (λ, Å)	Mo Kα (0.7093)
monochromator	graphite
2θ range, deg	4–40
temp, °C	15
hkl range of reflns	h = -27 to +27, k = 0 to +31, l = 0 to 16
no. of reflns measd	5930
no. of unique reflns	1695
with I > 3σ(I)	
computer programs	NRCVAX ^a on Silicon Graphics 4D-380
no. of variables in LS	198
k in w = 1/[σ ² (F _o) + kF _o ²]	0.0014
R, R _w , gof	0.071, ^b 0.097, ^b 1.80
density range in final Δ map, e Å ⁻³	-0.44 to +0.58
final shift/error ratio	0.024

^aGabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384. ^bR = [Σ||F_o - |F_c||]/[Σ|F_o|]; R_w = {[Σw|F_o - |F_c||²]/[Σ(w|F_o|²)]^{1/2}.

(s), 717 (m), 890 (s), 561 (s), 537 (s), 482 (w), 452 (w), 384 (m). Anal. Calcd for C₃₂H₂₄N₆P₂S₂Cl₂: C, 55.74; H, 3.51; N, 12.19; Cl, 10.28. Found: C, 55.87; H, 3.60; N, 12.32; Cl, 10.13.

Preparation of 9 (R = Ph, E = Se). Compound 8 (R = Ph) (3.0 g, 3.0 mmol) was added to a slurry of SeCl₄ [made in situ from selenium powder (0.522 g, 6.6 mmol)] in 20 mL of CH₃CN. The mixture was heated for a few minutes until all the reagents dissolved, and a clear canary yellow solution was produced. Almost immediately, a heavy yellow precipitate was formed. Subsequent filtration of this solid and recrystallization from CH₂Cl₂/CH₃CN mixture afforded canary yellow blocks of 9 (R = Ph, E = Se) [2.2 g, 93%; mp 193–195 °C; δ(P) 11.9 (in CH₂Cl₂)]. IR (cm⁻¹): 1461 (s), 1435 (m), 1377 (s), 1291 (s), 1264 (w), 1171 (m), 1126 (m), 1102 (w), 1017 (w), 943 (s), 914 (w), 969 (w), 800 (m), 757 (m), 728 (s), 702 (m), 672 (m), 538 (s). Anal. Calcd for C₃₂H₂₄N₆P₂Se₂Cl₂: C, 49.06; H, 3.09; N, 10.73; Cl, 9.05. Found: C, 49.28; H, 3.19; N, 10.56; Cl, 9.33.

Preparation of 4 (R = Ph, E = S). A slight excess of Ph₃Sb (0.63 g, 1.8 mmol) was added to a degassed solution of 9 (R = Ph, E = S) (1.1 g, 1.6 mmol) in 15 mL of benzonitrile. The mixture was heated to about a 100 °C, and a very deep red solution was obtained. Cooling the solution to room temperature afforded a red solid. Subsequent filtration and recrystallization from hot benzonitrile yielded irregular red blocks of 4 (R = Ph, E = S) [0.55 g, 54.7%; mp 235–239 °C; δ(P) 6.1]. IR (cm⁻¹): 1461 (s), 1377 (s), 1321 (w), 1282 (w), 1172 (m), 1114 (m), 983 (m), 857 (m), 921 (w), 854 (w), 811 (m), 755 (w), 740 (m), 725 (s), 689 (s), 555 (s), 539 (s), 485 (m), 450 (w). Anal. Calcd for C₃₂H₂₄N₆P₂S₂: C, 62.13; H, 3.91; N, 13.58; S, 10.36. Found: C, 62.44; H, 4.24; N, 13.51; S, 10.12.

Preparation of 4 (R = Ph, E = Se). A slight excess of Ph₃Sb (0.5 g, 1.4 mmol) was added to a degassed solution of 9 (R = Ph, E = Se) (1.0 g, 1.3 mmol) in a 1:1 mixture of CHCl₃ (15 mL) and toluene (15 mL). The solution immediately turned deep red. Cooling the solution to a room temperature afforded red microcrystals of 4 (R = Ph, E = Se) [0.61 g, 68%; mp 220–222 °C; δ(P) 8.1 (in CH₂Cl₂)]. IR (cm⁻¹): 1461 (s), 1377 (s), 1294 (s), 1097 (m), 1066 (w), 955 (m), 606 (m), 862 (w), 832 (s), 806 (m), 749 (w), 724 (s), 607 (m), 527 (s). Anal. Calcd for C₃₂H₂₄N₆P₂Se₂: C, 53.95; H, 3.40; N, 11.8. Found: C, 54.16; H, 3.51; N, 11.67. Larger crystals suitable for crystallographic analysis were grown by allowing two degassed solutions of 4 (R = Ph, E = Se) in CHCl₃ and of Ph₃Sb in CH₃CN to diffuse together very slowly through a small D-frit.

ESR Measurements. All ESR spectra were recorded on samples dissolved in degassed methylene chloride at ambient temperature with

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(14) Selenium tetrachloride was prepared by passing chlorine gas over a slurry of selenium powder in acetonitrile.

a Varian E109 ESR spectrometer. Samples were prepared either by in situ reduction of the corresponding chloride with triphenylantimony or by dissolving the radical dimer. Spectral simulations, from which hyperfine coupling constant data were extracted, were performed with a program written by Dr. U. M. Oehler, University of Guelph.⁸

X-ray Measurements. Table IV provides a summary of the pertinent crystallographic data. Crystals suitable for X-ray work were grown from $\text{CHCl}_3/\text{CH}_3\text{CN}$. However, the red blocks so obtained lost solvent rapidly; the data crystal was therefore mounted in the presence of a $\text{CH}_3\text{CN}/\text{CHCl}_3$ mixture inside a quartz capillary. For the cell determination, 25 reflections with 2θ in the range $15\text{--}35^\circ$ were measured. The Laue symmetry was shown to be $\bar{3}$ by an initial fast data collection over the entire reciprocal lattice with $2 < \theta < 6^\circ$. The systematic absences (hkl only present if $-h + k + l = 3n$) together with the Laue symmetry allow the space group to be $R\bar{3}$ or $R3$. E statistics indicated $R\bar{3}$, and this was confirmed by the analysis. The data were corrected for Lorentz, polarization, and absorption effects.¹⁵ The structure was solved by direct methods and refined by full-matrix least-squares calculations. With $Z = 9$, the dimer is required to have crystallographic inversion symmetry. Hydrogen atoms were clearly visible in difference maps computed at

intermediate stages of the analysis; they were allowed for as riding atoms [with $\text{C-H} = 0.95 \text{ \AA}$ and $U_{\text{iso}} = 1.1U(\text{C})$]. Only the phosphorus and selenium atoms were refined anisotropically. The presence of two CH_3CN molecules of solvation was noted; one solvent molecule was reasonably well located, but the other was disordered over at least two sites. These solvent atoms were allowed for by including them at the locations obtained from difference maps and allowing their U and occupancy factors to refine. Scattering factors including anomalous scattering were from standard sources.¹⁶

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Supplementary Material Available: Tables SI and SII, listing anisotropic thermal parameters and calculated hydrogen atom positions for **4** ($E = \text{Se}$) (2 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Chiral 18-Membered-Macrocyclic-Lanthanide Complexes: Circular Dichroism and Circularly Polarized Luminescence

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New chiral 18-membered lanthanide-macrocyclic complexes were prepared from lanthanide nitrates, 2,6-pyridinedicarboxaldehyde, and chiral 1,2-diaminocyclohexane by template reaction, where the lanthanides are lanthanum(III), europium(III), and terbium(III) ions. The structures of these complexes were characterized by NMR and luminescence spectroscopy to have D_2 molecular symmetry. Strong circularly polarized luminescence was also detected for the Eu(III) and Tb(III) complexes due to the twisted conformation. The absolute chiral structures were determined from CD data. The intramolecular energy-transfer processes were found to occur between π^* electronic states of the ligand and 4f levels of the central lanthanide ions in the Eu(III) and Tb(III) complexes. In addition, a photodecomposition reaction was studied under strong UV laser radiation.

Introduction

Luminescence and circularly polarized luminescence (CPL) spectra are powerful tools to investigate the structures and electronic states of lanthanide complexes in solution.^{1,2} However, chiral lanthanide complexes were often found to be in equilibrium with some solvated species or geometrical isomers coexisting in solution. In such a system, it is in principle difficult to study exact chiroptical properties of the complexes even by the sensitive spectroscopic techniques.

In recent years, new lanthanide complexes having 18-membered macrocyclic ligands have been reported by several groups.³ These complexes are relatively easily prepared by using a template reaction of 2,6-dicarbonylpyridine derivatives and diamines in the presence of lanthanide ions. It is quite reasonable to consider that the macrocyclic complex does have more symmetric and rigid structure than the other complexes containing flexible linear ligands. When chiral diamines were used, a series of chiral ligands could be prepared by template syntheses. Therefore, the chiral

macrocyclic complexes are very good materials suited for studying the chiroptical properties of lanthanide complexes in solution. We report the synthesis and spectroscopic study of the chiral macrocyclic lanthanide complexes $\text{Ln}(\text{RR-pydach})^{3+}$ and $\text{Ln}(\text{SS-pydach})^{3+}$ including two *trans*-1,2-diaminocyclohexane moieties ($\text{RR-pydach} = 4(R),9(R),19(R),24(R)$ -3,10,18,25,31,32-hexaazapentacyclo[25.3.1.1^{12,24}.0^{4,9}.0^{19,24}]-dotriaconta-1-(31),2,10,12,14,16(32),17,25,27,29-decaene and SS-pydach is an enantiomer having 4(*S*),9(*S*),19(*S*),24(*S*) configurations; $\text{Ln} = \text{Eu, Tb, and La}$). The structures of the macrocyclic complexes are shown in Figure 1. In the course of our study, photophysical properties of the achiral Eu^{3+} macrocyclic complex $\text{Eu}(\text{pyMeen})^{3+}$ were reported by Sabbatini et al.,⁴ where $\text{pyMeen} = 2,7,13,18$ -tetramethyl-3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]tetracosane-1(23),2,6,8,10,12(24),13,17,19,21-decaene. In this paper, spectroscopic properties of $\text{Eu}(\text{pyMeen})^{3+}$, are also compared with our complexes.

Experimental Section

Lanthanide nitrate hexahydrates were prepared as follows. Lanthanide oxides were dissolved in an excess of nitric acid. The solution was evaporated on a steam bath to give a syrup. After cooling, white crystals obtained were dried in a desiccator and used without further purification. Optical resolution of *trans*-1,2-diaminocyclohexane was performed by using L- and D-tartaric acid.⁵ Pyridine-2,6-dicarboxaldehyde was synthesized from 2,6-pyridinedimethanol⁶ or purchased

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