Studies on Organolanthanide Complexes. Part 56.[1] Formation of Ion-pair Complexes $[Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot$phen (Ln = La, Pr or Nd; phen = 1,10-phenanthroline) and Crystal Structure for Ln = Pr†

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In the presence of 1,10-phenanthroline (phen), lanthanide chlorides $LnCl_3$ reacted with cyclopentadienylsodium to give the novel complexes $[Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot$phen (Ln = La, Pr or Nd). In the praseodymium case, crystal structure analysis showed that the complex was an organolanthanide ion pair. In the anion the central metal is co-ordinated to three cyclopentadienyl rings and a chlorine atom, forming a distorted tetrahedron. In the cation the sodium atom is co-ordinated to six nitrogen atoms from three phenanthrolines, to form a distorted octahedron.

The complexes $[Ln(C_5H_5)Cl_2]$ have recently received considerable attention.[2-8] as they are important precursors for synthesis of organolanthanide alkyl or hydride species. However, the lighter lanthanides, which have larger ionic radii, produce co-ordinatively unsaturated complexes which are unstable. We attempted to synthesize the lighter monocyclopentadienyllanthanide dichlorides by use of the co-ordination effect between the lanthanide metal and 1,10-phenanthroline but new complexes containing anions $[Ln(C_5H_5)_3Cl]^-$ were unexpectedly formed. Complexes containing the unit $[Ln(C_5H_5)_3X]^-$ (X = alkyl or halide) are rare,[9] but many complexes containing di- or poly-lanthanide anionic units have been reported such as $[(C_5H_5)_3LnHLn(C_5H_5)_3]^-$,[10,11] $[(C_5H_5)_3LnNNNLn(C_5H_5)_3]^-$,[12] $[(C_5H_5)_3LnClLn(C_5H_5)_3]^-$,[12] $[(C_9H_7)_3LnClLn(C_9H_7)_3]^-$ [13] and $[\{Ln(C_5H_5)_3\}_3H]^-$.[14,15]

Herein we report the formation of organolanthanide ion-pair complexes $[Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot$phen (Ln = La, Pr or Nd) and the crystal structure of $[Na\cdot 3phen]^+[Pr(C_5H_5)_3Cl]^-\cdot$phen.

Results and Discussion

Formation of Complexes $[Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot$phen.—The new complexes $[Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot$phen (Ln = La **1**, Pr **2** or Nd **3**) were afforded by a one-pot reaction of $LnCl_3$, $Na(C_5H_5)$ and phen in the molar ratio 1 : 1 : 1. Their formation [tetrahydrofuran (thf), room temperature] may involve three steps as shown in equations (1)–(3). First the

$$LnCl_3 + Na(C_5H_5) \longrightarrow [Ln(C_5H_5)Cl_2]\cdot 3thf + NaCl \quad (1)$$

$$3[Ln(C_5H_5)Cl_2]\cdot 3thf \longrightarrow [Ln(C_5H_5)_2]\cdot thf + 2LnCl_3 \quad (2)$$

$$[Ln(C_5H_5)_3]\cdot thf + NaCl \xrightarrow{phen} [Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot phen \quad (3)$$

reaction of $LnCl_3$ and $Na(C_5H_5)$ produces the unstable complex $[Ln(C_5H_5)Cl_2]\cdot$3thf, which rearranges to $[Ln(C_5H_5)_3]\cdot$thf; finally, in the presence of phen, the reaction of $[Ln(C_5H_5)_3]\cdot$thf and NaCl yields the new complexes $[Na\cdot 3phen]^+[Ln(C_5H_5)_3Cl]^-\cdot$phen, similar to $[Ln(C_5H_5)_3]$ with NaCl in the presence of 1,2-dimethoxyethane (dme).[12]

Table 1 Crystallographic data for $[Na\cdot 3phen][Pr(C_5H_5)_3Cl]^-\cdot$phen **2**

Formula	$C_{63}H_{47}ClN_8NaPr$
M	1115.5
T/K	298
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Crystal size/mm	0.5 × 0.40 × 0.30
a/Å	14.059(4)
b/Å	15.941(5)
c/Å	12.761(4)
α/°	108.43(2)
β/°	104.86(2)
γ/°	85.47(2)
U/Å^3	2622.2(3)
D_c/g cm^{-3}	1.41
Z	2
Data collected	$\pm h, \pm k, +l$
2θ range/°	$3 < 2\theta < 50.0$
Total reflections	7360
Independent reflections	6848
No. of observed data [$F > 3\sigma(F)$]	4750
F(000)	1136
R, R'	0.035, 0.032
Goodness of fit	1.15

The new complexes **1–3** were recrystallized from thf, to give crystals of different colours depending on the lanthanide metal present. They can be dissolved in thf, but their solubilities are lower than that of $[Ln(C_5H_5)_3]$.

Proton NMR for complex **1** were measured in perdeuteriotetrahydrofuran. The resonance at δ 5.90 can be assigned to the protons on the cyclopentadienyl rings, and those at δ 7.70–8.95 to the protons of phen. It is noteworthy that the latter signals are shifted to lower field compared with those of unco-ordinated phen.[16] This result showed that phen was co-ordinated to the metals (La or Na). X-Ray structure analysis of complex **2** revealed that it is co-ordinated to the sodium atom.

Structure of $[Na\cdot 3phen]^+[Pr(C_5H_5)_3Cl]^-\cdot$phen **2**.—The crystallographic details, atomic coordinates and selected bond lengths and angles of complex **2** are listed in Tables 1–3. The

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pr	1 808(1)	1 743(1)	4 597(1)	C(31)	7 415(4)	1 809(3)	3 966(4)
Cl	1 068(1)	2 746(1)	3 144(1)	C(32)	8 013(4)	1 799(4)	3 195(5)
Na	6 950(2)	4 005(1)	7 213(2)	C(33)	8 470(4)	2 516(4)	3 278(5)
C(1)	350(4)	2 278(4)	5 846(4)	C(34)	8 390(4)	3 353(4)	4 141(4)
C(2)	1 017(4)	1 789(4)	6 429(4)	C(35)	8 811(4)	4 125(4)	4 186(5)
C(3)	1 897(4)	2 270(4)	6 919(4)	C(36)	8 703(4)	4 885(4)	5 002(5)
C(4)	1 764(4)	3 053(4)	6 643(4)	C(37)	8 168(4)	4 864(4)	5 791(5)
C(5)	802(4)	3 058(4)	5 980(4)	C(38)	7 867(3)	3 381(3)	4 943(4)
C(6)	1 429(4)	272(3)	2 602(4)	C(39)	7 345(3)	2 596(3)	4 855(4)
C(7)	487(4)	575(3)	2 726(5)	C(40)	1 601(4)	7 513(3)	1 731(5)
C(8)	358(4)	386(3)	3 681(5)	C(41)	1 014(4)	7 875(4)	908(5)
C(9)	1 202(4)	−17(3)	4 129(5)	C(42)	591(4)	7 333(4)	−125(5)
C(10)	855(4)	−90(3)	3 464(4)	C(43)	739(4)	6 406(3)	−370(4)
C(11)	3 610(4)	1 395(4)	3 988(5)	C(44)	263(4)	5 786(3)	−1 437(4)
C(12)	3 793(4)	1 285(4)	5 075(5)	C(45)	359(4)	4 927(4)	−1 616(4)
C(13)	3 788(4)	2 116(4)	5 852(5)	C(46)	978(4)	4 569(3)	−762(4)
C(14)	3 578(4)	2 730(4)	5 253(5)	C(47)	1 097(4)	3 668(4)	−931(4)
C(15)	3 485(4)	2 288(4)	4 124(5)	C(48)	1 695(4)	3 379(3)	−95(5)
C(16)	5 384(4)	733(4)	2 729(5)	C(49)	2 188(4)	4 012(3)	926(4)
C(17)	6 195(4)	922(4)	8 552(5)	C(50)	1 480(3)	5 156(3)	289(4)
C(18)	6 287(4)	1 125(4)	9 663(5)	C(51)	1 339(4)	6 102(3)	494(4)
C(19)	5 387(4)	1 132(3)	9 956(4)	C(52)	4 381(5)	6 711(4)	1 330(5)
C(20)	5 320(4)	1 360(4)	11 117(5)	C(53)	5 128(6)	6 737(4)	777(5)
C(21)	4 431(5)	1 411(4)	11 392(5)	C(54)	5 843(5)	6 155(4)	790(5)
C(22)	3 565(4)	1 205(3)	10 514(5)	C(55)	5 878(4)	5 520(4)	1 351(4)
C(23)	2 656(4)	1 241(4)	10 773(5)	C(56)	6 622(4)	4 853(4)	1 380(5)
C(24)	1 817(4)	979(4)	9 889(5)	C(57)	6 615(4)	4 260(4)	1 885(5)
C(25)	1 928(4)	710(4)	8 779(5)	C(58)	6 861(4)	4 249(4)	2 470(4)
C(26)	3 588(4)	930(3)	9 359(4)	C(59)	5 822(4)	3 642(4)	3 043(5)
C(27)	4 526(4)	919(3)	9 077(4)	C(60)	5 130(4)	3 702(4)	3 603(5)
C(28)	6 253(4)	1 966(4)	5 430(5)	C(61)	4 431(4)	4 379(4)	3 586(5)
C(29)	6 272(4)	1 161(4)	4 592(5)	C(62)	5 124(4)	4 909(3)	2 487(4)
C(30)	6 859(4)	1 072(3)	3 873(4)	C(63)	5 121(4)	5 539(3)	1 897(4)
N(1)	4 537(3)	732(3)	7 969(4)	N(5)	1 779(3)	6 662(3)	1 537(3)
N(2)	2 764(3)	687(3)	8 504(4)	N(6)	2 087(3)	4 874(3)	1 125(3)
N(3)	6 774(3)	2 664(3)	5 585(3)	N(7)	4 379(3)	6 138(3)	1 881(3)
N(4)	7 754(3)	4 137(3)	5 764(3)	N(8)	4 416(3)	4 958(3)	3 050(3)

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Pr–C(1)	2.830(6)	Pr–C(2)	2.874(6)
Pr–C(3)	2.784(5)	Pr–C(4)	2.792(5)
Pr–C(5)	2.824(5)	Pr–Cent 1[a]	2.545
Pr–C(6)	2.872(4)	Pr–C(7)	2.842(5)
Pr–C(8)	2.842(5)	Pr–C(9)	2.831(5)
Pr–C(10)	2.825(5)	Pr–Cent 2	2.575
Pr–C(11)	2.802(6)	Pr–C(12)	2.790(5)
Pr–C(13)	2.836(5)	Pr–C(14)	2.844(6)
Pr–C(15)	2.841(6)	Pr–Cent 3	2.564
Pr–Cl	2.775(2)	Na–N(3)	2.441(4)
Na–N(4)	2.469(5)	Na–N(5′)[b]	2.485(5)
Na–N(6′)	2.457(4)	Na–N(7′)	2.494(6)
Na–N(8′)	2.460(5)		
Cent 1–Pr–Cent 2	117.0	Cent 1–Pr–Cl	104.5
Cent 2–Pr–Cent 3	117.7	Cent 2–Pr–Cl	99.8
Cent 1–Pr–Cent 3	114.9	Cent 3–Pr–Cl	98.8
N(3)–Na–N(4)	67.6(2)	N(3)–Na–N(5′)	93.1(1)
N(3)–Na–N(6′)	153.4(2)	N(3)–Na–N(7′)	103.5(2)
N(3)–Na–N(8′)	112.0(1)	N(4)–Na–N(5′)	104.7(2)
N(4)–Na–N(6′)	98.5(2)	N(4)–Na–N(7′)	159.8(1)
N(4)–Na–N(8′)	98.6(2)	N(5′)–Na–N(6′)	67.6(1)
N(5′)–Na–N(7′)	96.2(2)	N(5′)–Na–N(8′)	150.8(2)
N(6′)–Na–N(7′)	96.2(2)	N(6′)–Na–N(8′)	92.0(1)
N(7′)–Na–N(8′)	67.0(2)		

[a] Cent is the centroid of the cyclopentadienyl ring. [b] Primed atoms are related to unprimed ones by the symmetry transformation $1 - x, 1 - y, 1 - z$.

molecular structure and molecular packing in the unit cell are shown in Figs. 1 and 2. The complex consists of an ion pair, the cation $[Na{\cdot}3phen]^+$ and the anion $[Pr(C_5H_5)_3Cl]^-$, and one independent phen molecule.

In the anion $[Pr(C_5H_5)_3Cl]^-$ a distorted tetrahedron around the praseodymium ion is formed with three centroids of the cyclopentadienyl rings and a chlorine atom. The average Pr–C(η^5) bond distance is 2.822 Å, similar to the value reported for $[Pr(C_5H_5)_3]{\cdot}$thf, 2.80 Å.[17] Since the ionic radius of Pr^{3+} is about 0.016 Å larger than that of Nd^{3+},[18] the value is comparable with the bond distance [2.826 Å, Nd–C(η^5)] in $[Li{\cdot}3dme][Nd(C_5H_5)_3Ph]$.[9] The Pr–Cl bond length [2.775(2) Å] is in good agreement with that [2.718(6) Å] in the compound $[Pr(C_5H_4Bu^t)_2Cl]{\cdot}2$thf.[19] It is interesting to compare this distance with those of bridging Ln–Cl–Ln in the anions $[(C_5H_5)_3SmClSm(C_5H_5)_3]^-$ (2.82 Å)[12] and $[(C_9H_7)_3NdCl\text{-}Nd(C_9H_7)_3]^-$ (2.831 Å).[13] Significantly the value in **2** is shorter than in these two anions even when the differences in ion radii are taken into account.[18] It may be that the terminal interactions between Ln^{3+} and Cl^- are stronger than that in corresponding bridging interactions. Similar behaviour has been observed for ytterbium complexes with bridging $Yb(\mu\text{-}Cl)_2Yb$ [Yb–Cl 2.628(2) and 2.647(2) Å][20] or terminal Yb–Cl (Yb–Cl 2.539 Å).[19]

The cation consists of one sodium atom and three phen molecules. Each sodium atom is co-ordinated by six nitrogen atoms forming a six-co-ordinated distorted octahedron with average Na–N 2.468 Å; the nitrogen atoms involved are N(3), N(4), N(5′), N(6′), N(7′) and N(8′), where primed atoms are related to unprimed ones by the symmetry transformation $1 - x, 1 - y, 1 - z$.

In conclusion, the reaction of lanthanide chloride and cyclopentadienylsodium in the presence of phen produced a

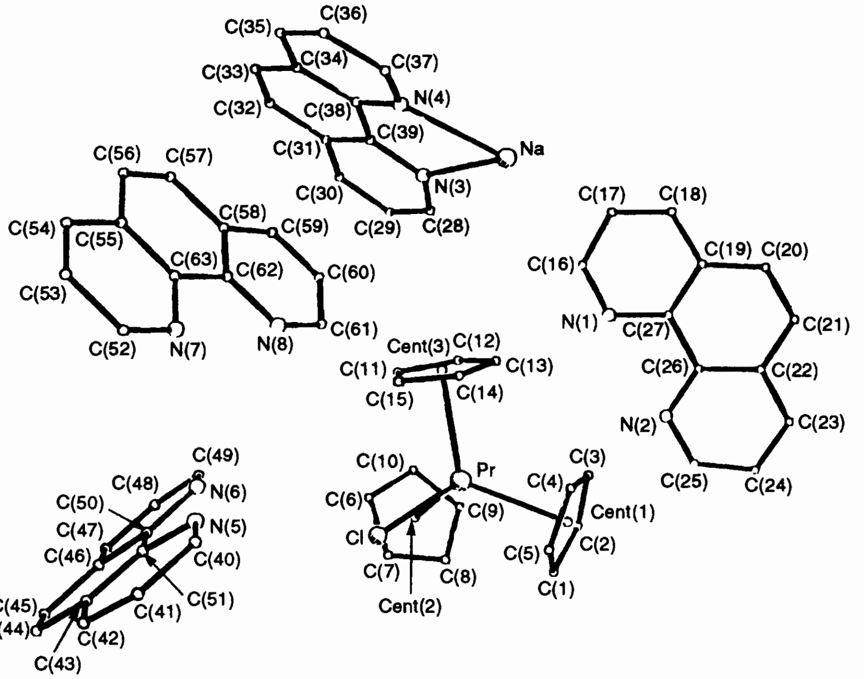

Fig. 1 Molecular structure of $[Na{\cdot}3phen]^+[Pr(C_5H_5)_3Cl]^-{\cdot}phen$ **2**

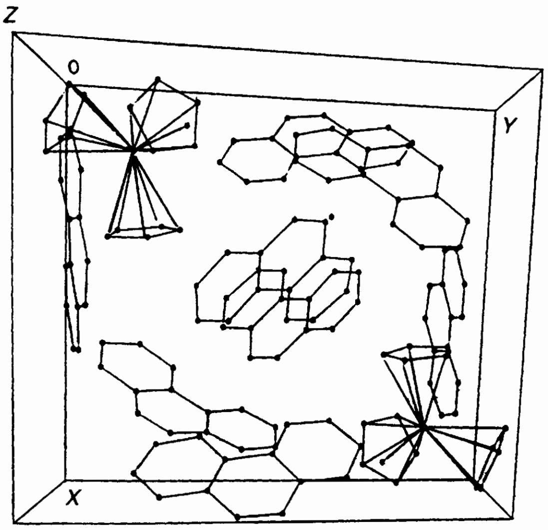

Fig. 2 Packing of $[Na{\cdot}3phen]^+[Pr(C_5H_5)_3Cl]^-{\cdot}phen$ in the unit cell

novel type of complex. X-Ray structural investigations showed that the new complexes contained monolanthanide units. This is different from previous complexes, which contain di- or poly-lanthanide anions. The average Ln–C(η^5) bond distance in the monolanthanide unit is in good agreement with that in the dilanthanide units, but the Ln–Cl bond distance in the former is shorter than in the latter.

Experimental

All operations were performed under purified argon by using Schlenk techniques. Solvents were refluxed and distilled either over finely divided $LiAlH_4$ or blue sodium–benzophenone under argon immediately before use. Sodium cyclopentadienide was prepared by the usual method. 1,10-Phenanthroline was dried by sublimination. The IR spectra were recorded on Perkin-Elmer 983 and Digilab FTIS-20/E Fourier-transform spectrometers with Nujol and Fluorolube mulls and were examined between disc-shaped CsI crystals. Proton NMR spectra were obtained on a FX-90Q (90 MHz) spectrometer referenced to external $SiMe_4$ in $[^2H_8]$thf.

Metal analyses for the complexes were accomplished using a direct complexometric titration with disodium ethylenediaminetetraacetate. Carbon, hydrogen and nitrogen analyses were performed by the combustion method in an aluminium tube.

Preparation of Organolanthanide Ion-pair Complexes.— $[Na{\cdot}3phen]^+[La(C_5H_5)_3Cl]^-{\cdot}phen$ **1**. A thf solution (10.0 cm^3) of 0.39 mol dm^{-3} cyclopentadienylsodium was added slowly to a suspension of $LaCl_3$ (0.93 g, 3.8 mmol) and phen (0.75 g, 4.1 mmol) in thf (30 cm^3) at room temperature. After stirring for 20 h at room temperature, the Schlenk flask was centrifuged and the precipitate was separated from the solution, which was reduced in volume to about 15 cm^3. Addition of hexane (2 cm^3) was added and the solution cooled at 0 °C to give 0.85 g of colourless crystals of the product (60%) (Found: C, 68.00; H, 4.55; La, 11.95; N, 10.25. $C_{63}H_{47}ClLaN_8Na$ requires C, 67.95; H, 4.25; La, 12.45; N, 10.05%); $\delta_H([^2H_8]thf)$ 5.90 (15 H, s, C_5H_5) and 7.70–8.95 (32 H, m, phen); IR(cm^{-1}): 3036s, 2960s, 2343s, 1804s, 1615s, 1584s, 1560s, 1504s, 1446s, 1419s, 1040s, 1018s, 980m, 905s, 840m, 768s, 733s, 708m, 650m, 590s, 440m and 286s.

$[Na{\cdot}3phen]^+[Pr(C_5H_5)_3Cl]^-{\cdot}phen$ **2**. This compound was prepared from $PrCl_3$ (1.01 g, 4.1 mmol), phen (0.75 g, 4.1 mmol) and a solution (10.5 cm^3) of 0.39 mol dm^{-3} cyclopentadienylsodium in thf (30 cm^3) using the procedure described above. Yellow crystals were obtained: yield 1.01 g, 66% (Found: C, 68.45; H, 4.05; N, 10.05; Pr, 12.05. $C_{63}H_{47}ClN_8NaPr$ requires C, 67.85; H, 4.20; N, 10.05; Pr, 12.65%); IR(cm^{-1}): 3026s, 2960s, 1585s, 1560s, 1444s, 1417s, 1039s, 1017s, 840s, 766s, 708m, 650s, 590s, 438m and 292m.

$[Na{\cdot}3phen]^+[Nd(C_5H_5)_3Cl]^-{\cdot}phen$ **3**. This compound was prepared from $NdCl_3$ (0.58 g, 2.4 mmol), phen (0.46 g, 2.4 mmol) and a solution (6.0 cm^3) of 0.39 mol dm^{-3} cyclopentadienylsodium in thf (15 cm^3) using the procedure described above. Blue crystals were obtained: yield 0.41 g, 45% (Found: C, 67.45; H, 4.25; N, 10.45; Nd, 12.65. $C_{63}H_{47}ClN_8NaNd$ requires C, 67.65; H, 4.25; N, 10.00; Nd, 12.90%); IR(cm^{-1}): 3024s, 2964s, 1615s, 1588s, 1582s, 1560s, 1443s, 1417s, 1039s, 1018s, 846s, 764s, 733s, 436m and 288s.

Crystal Structure Determination of Complex **2**.—A suitable single crystal was sealed under argon in a thin-walled glass capillary. Intensity data were collected on a Nicolet R3M/E diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) in the ω-scan mode. Final lattice parameters were obtained by a least-squares refinement of the 2θ values of 25 reflections. The choice of space group $P\bar{1}$ (no. 2) was confirmed by the successful refinement. The crystallographic parameters are listed in Table 1. The intensities were corrected for Lorentz polarization and absorption effects. The position of praseodymium was revealed by a Patterson map and all non-hydrogen atoms were derived on successive Fourier synthesis. All positional parameters and thermal parameters for non-hydrogen atoms were refined anisotropically. Calculations were made on an Eclipse S/140 minicomputer with the SHELX 76 program system.[21] The final atomic coordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Financial support of this project by the Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Academia Sinica is gratefully acknowledged.

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Received 14*th January* 1994; *Paper* 4/00228H