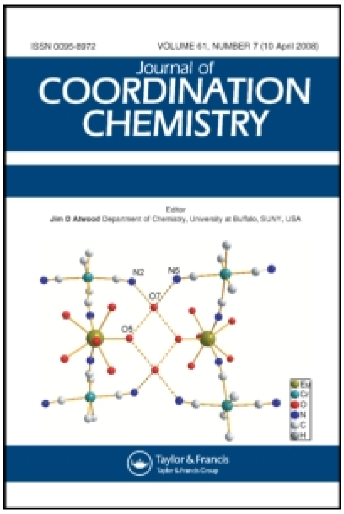

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Synthesis, Structure and Spectroscopy of the Complexes Tetrakis μ-Trichloroacetato)Bis[Trichloroacetato-Ethanol-(1,10-Phenanthroline-*N,N'*)LN(III)] (LN = Pr, Nd and Er)

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SYNTHESIS, STRUCTURE AND SPECTROSCOPY OF THE COMPLEXES TETRAKIS (μ-TRICHLOROACETATO)BIS[TRICHLOROACETATO-ETHANOL-(1,10-PHENANTHROLINE-*N*,*N′*)Ln(III)] (Ln = Pr, Nd AND Er)

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Tetrakis(μ-trichloroacetato)bis[trichloroacetatoethanol-(1,10-phenanthroline-*N*,*N′*)Ln(III)] (Ln = Pr, Nd and Er) complexes have been synthesized and their crystal structures have been determined by X-ray diffraction at reduced temperatures. The three structures are isomorphous: monoclinic, $P2_1/c$. For the praseodymium complex, $a = 12.418(6)$, $b = 18.444(5)$, $c = 17.742(9)$ Å, $\beta = 131.71(3)°$, $R = 0.051$, and $R_w = 0.057$. For the neodymium complex $a = 12.396(6)$, $b = 18.498(4)$, $c = 17.339(8)$ Å, $\beta = 131.50(2)°$, $R = 0.054$, and $R_w = 0.060$. For the erbium complex $a = 12.186(3)$, $b = 18.462(4)$, $c = 17.478(4)$ Å, $\beta = 131.12(1)°$, $R = 0.041$, and $R_w = 0.045$. Each lanthanide ion is coordinated by four bridging bidentate trichloroacetate ligands, one monodentate trichloroacetate ligand, one ethanol ligand and one phenanthroline ligand, yielding a distorted square antiprismatic configuration. The two lanthanide ions are connected by the four bridging bidentate trichloroacetate ligands to form a dimer. The NMR spectra of the complexes confirm the coordination of ethanol ligands to the lanthanide ions.

Keywords: Lanthanides, crystal structure, phenanthroline, complexes, synthesis

INTRODUCTION

The complexes of lanthanides (Ln) with 1,10-phenanthroline have been studied by Hart and Laming[1] and Lobanov and Smirnova.[2,3] Syntheses and spectroscopic analyses of some of these complexes have been carried out by Spacu and Antonescu.[4–6] In studies of the extraction of lanthanide ions (Ln^{3+}) from aqueous solutions with trichloroacetate anions and a series of bidentate heterocyclic amine ligands, including 1,10-phenanthroline, Ni and coworkers[7–10] have demonstrated correlations between the atomic number and the distribution ratio of lanthanide ions in solution for all systems. Some heterocyclic amine lanthanide complexes possess fluorescence properties which are believed to be caused by the coupling of the *f*-electrons of the central ion and the π-electrons of the heterocyclic ligand. However, a full understanding of the chemistry of these compounds is limited by an absence of

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structural information. The structure of tris(acetylacetonato)(1,10-phenanthroline) Europium(III) has, however, been reported.[11]

Structural studies of lanthanide complexes involving carboxylate ligands have shown that the lanthanide ions have several types of coordination and that coordination numbers are usually 8 or 9. The type of coordination depends both on the size and character of the ligands and on the size of the central ion.[12-14] Heavy lanthanide complexes usually have fewer ligands than light lanthanide complexes of the same ligands.[12-15]

The carboxylate ligand has various modes of coordination to lanthanide ions [12-13]: (i) the monodentate mode, in which an oxygen atom of the carboxylate coordinates to a central ion; (ii) the bidentate mode, in which the two oxygen atoms of a carboxylate coordinate to one central atom; (iii) the bridging bidentate mode, in which the two oxygen atoms of a carboxylate coordinate to two separate central atoms; (iv) the bridging terdentate mode, in which the two oxygen atoms of a carboxylate coordinate to a central atom and one of the oxygen atoms coordinates to a second central atom. The bridging coordination modes are only found in dimers or polymeric lanthanide complexes.[12-14]

The present investigation of the three lanthanide complexes $[(CCl_3COO^-)_3(phen)(C_2H_5OH)Ln^{3+}]_2$ (Ln = praseodymium, neodymium and erbium; phen = 1,10-phenanthroline) is part of a continuing study of trichloroacetate lanthanide complexes with a series of heterocyclic amine ligands. We report here their synthesis, spectroscopic data, thermal analysis and structures.

EXPERIMENTAL

Synthesis

All complexes were prepared in a similar manner by dissolving the lanthanide oxide in 6 M HCl, then adding trichloroacetate ($Ln{:}CCl_3COOH = 1{:}1.4$ mole ratio) to the solution of lanthanide chloride. After trichloroacetic acid was completely dissolved in the solution, the solution was slowly evaporated. The dry residue was dissolved in ethanol:chloroform (1:1) to obtain a solution of lanthanide trichloroacetate. The lanthanide solution was mixed with a solution of 1,10-phenanthroline (Ln:phen = 1:1 mole ratio) in ethanol:chloroform:tetrahydrofuran (1:6:1). After two days, single crystals of a complex were obtained from the final solution through slow evaporation. Most of the original lanthanide was recovered in the complex. *Anal.*: Calcd. for $[(CCl_3COO^-)_3(phen)(C_2H_5OH)Pr^{3+}]_2$: C, 28.11; H, 1.65; N, 3.13; Pr, 16.49; Cl, 37.34%. Found: C, 28.18; H, 1.72; N, 3.22; Pr, 16.52; Cl, 38.01%. Calcd. for $[(CCl_3COO^-)_3(phen)(C_2H_5OH)Nd^{3+}]_2$: C, 28.00; H, 1.64; N, 3.27; Nd, 16.82; Cl, 37.19%. Found: C, 27.81; H, 1.71; N, 3.15; Nd, 16.77; Cl, 37.32%. Calcd. for $[(CCl_3COO^-)_3(phen)(C_2H_5OH)Er^{3+}]_2$: C, 27.27; H, 1.60; N, 3.17; Er, 18.99; Cl, 36.22%. Found: C, 27.32; H, 1.76; N, 3.13; Er, 18.79; Cl, 36.16%.

Differential Thermoanalysis

The results from differential thermoanalysis of each complex are listed in Table I. Endothermic peaks in the thermograms indicate the loss of C_2H_5OH from the complexes and exothermic peaks indicate the decomposition of the complexes. All complexes decomposed below their melting points.

TABLE I
Differential thermoanalysis peaks observed for the complexes.

Complex	Temperatures (°C)	
	Endothermic	Exothermic
Pr complex	88	200
Nd complex	93	203
Er complex	120	221

Spectroscopic measurements

The NMR spectra of the complexes in dimethyl sulfoxide were obtained on an FT-80A spectrometer at 70°C. The results are given in Table II. The absorption bands of the IR spectra are listed in Table III.

TABLE II
NMR spectral data for the complexes (ppm).

Complex	Pr	Nd	Er
$-CH_3$	0.97, 1.05, 1.14	0.98, 1.07, 1.14	1.00, 1.08, 1.16
$-CH_2$	3.30–3.60	3.30–3.55	3.35–3.60
$-OH$	4.17	4.16	4.15

TABLE III
Selected IR data (cm^{-1}; KBr pellet) for the complexes.

Complex	ν_{as} O–C=O	ν_s O–C=O	ν C=N, C=C	ν O–H
CCl_3COO^-	1775(vs)			
1,10-phenanthroline			1590(m) 1530(s)	
Pr complex	1708(vs)	1420(s)	1580(m) 1510(s)	3478(s)
Nd complex	1710(vs)	1420(s)	1580(m) 1510(s)	3478(s)
Er complex	1720(vs)	1422(s)	1581(m) 1515(s)	3480(s)

Crystal structure determinations

The space groups and the approximate lattice constants of the crystals were determined from precession photographs of the crystals. The densities of the crystals were measured by the flotation method in a mixture of iodoform and hexane. The observed densities indicated that the asymmetric unit contains half a formula unit.

Intensity data was collected on a modified Picker four-circle diffractometer controlled by the NRCC diffractometer system[17] using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å).

TABLE IV
Crystal data and structure refinement parameters.

	Pr complex	Nd complex	Er complex
formula	$C_{40}H_{28}Cl_{18}N_4O_{14}Pr_2$	$C_{40}H_{28}Cl_{18}N_4Nd_2O_{14}$	$C_{40}H_{28}Cl_{18}Er_2N_4O_{14}$
m.w.	1708.58	1715.24	1761.28
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
crystal dimensions (mm)	0.30 × 0.24 × 0.24	0.35 × 0.31 × 0.24	0.47 × 0.36 × 0.34
colour	light green	light red	pink
a (Å)	12.418(6)	12.396(6)	12.186(3)
b (Å)	18.444(5)	18.498(4)	18.462(4)
c (Å)	17.742(9)	17.339(8)	17.478(4)
β (°)	131.71(3)	131.50(2)	131.12(1)
Z	2	2	2
V (Å^3)	3033(2)	3046(2)	2962(1)
F(000)	1664	1668	1700
ρ_{obs} (g cm^{-3})	1.89	1.84	1.98
ρ_{cal} (g cm^{-3})	1.87	1.87	1.97
μ (cm^{-1})	24.11	25.16	37.93
number of reflections used for lattice constant refinements	40	32	42
temperature (°C)	−46	−73	−52
number of measured reflections	3954	3987	3891
number of reflections used in structure refinements ($I \geq 2\sigma(I)$)	3459	3373	3533
number of least-squares variables	339	339	388
2θ range (°)	3.0–45.0	3.0–45.0	3.0–45.0
R	0.051	0.054	0.041
R_w†	0.057	0.060	0.045
S	1.169	1.123	0.715

† $R_w = \left(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\right)^{1/2}$.

Lattice constants were determined by least-squares refinement using Mo$K\alpha_1$ radiation ($\lambda = 0.70926$ Å). One independent set of reflections was collected for each crystal. A modified Enraf-Nonius universal low temperature device was used for cooling the specimens. All crystals were coated with collodion to prevent direct contact with air and water, in the presence of which they decompose.

The faces and dimensions of the crystals were measured and the intensities of the reflections were corrected for absorption effects using the Gaussian integration method. All calculations were performed using the XTAL system of crystallographic programs.[18] Lorentz-polarization corrections were applied. The variances of the intensities were estimated from combined counting statistics and the machine instability factor. The structure amplitudes and their standard deviations were calculated from the resulting intensities and their variances. For reflections with $I < 3\sigma(I)$, including those for which negative values were observed for I, Baysian statistics were used to calculate the structure amplitudes and their standard deviations.

Only reflections with $I > 2\sigma(I)$ were used in the refinements. In the structure determinations, the positions of the lanthanide ions were located from Patterson maps and refined by least-squares methods with isotropic temperature factors. The other atoms were found by Fourier syntheses. After all the expected non-hydrogen atoms were found, least-squares refinements were carried out with anisotropic temperature factors. For the Pr complex and the Nd complex the ethanol ligands showed distorted structures which are assumed to be the result of disorder. The positions of the hydrogen atoms were found from difference Fourier syntheses or were calculated based on the known atomic configurations of the attached atoms and assuming C–H and O–H bond lengths of 1.0 Å. The final refinements of the structures were carried out by full-matrix least-squares methods with anisotropic temperature factors for the non-hydrogen atoms and with isotropic temperature factors for hydrogen atoms, and using fixed anomalous dispersion terms for the Pr, Nd, Er, and Cl atoms. In the Pr complex and the Nd complex, the ethanol ligands were refined as rigid bodies with invariant isotropic temperature factors. The least-squares weights for the refinements were estimated by the REGWT method.[18,19] The crystal data and refinement parameters for the three structures are listed in Table IV. Lists of (i) atom coordinates and isotropic temperature factors, (ii) anisotropic temperature factors for the non-hydrogen atoms, (iii) bond lengths and bond angles, and (iv) observed and calculated structure factors for the three complexes are available from B.E.R.

RESULTS

The coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms and their estimated standard deviations for the three complexes are listed in Tables V to VII. Bond lengths, bond angles and their estimated standard deviations were calculated using the variances and covariances of the atom coordinates with the program REGFE.[18] The structures are isomorphous. Important structural parameters are given in Table VIII. A stereoscopic view of the erbium dimer is given in Figure 1 and the atomic numbering scheme for the central fragment of the dimers is given in Figure 2.

NMR spectra clearly show the presence of the ethanol molecule in the crystals. Furthermore, the difference between the chemical shift of the OH proton in the complexes and in free ethanol suggests that the proton of the OH group in the complexes is deshielded due to coordination of the O atom to the lanthanide ion.

The coordination of the lanthanide ion in Figure 1 shows a distorted square antiprismatic configuration and two lanthanide ions are connected through four bridging bidentate trichloroacetate ligands to form a dimer. The complex dimer contains a centre of symmetry. For each lanthanide ion, four O atoms of the four bridging bidentate trichloroacetates occupy the ligand sites of a square face of the square antiprism and the deviations of the O atoms from their least-squares plane are negligible. The O atom of the monodentate trichloroacetate ligand, the O atom of the ethanol ligand and the two N atoms of the bidentate phenanthroline ligand occupy the ligand sites of the other square face of the antiprism, but the deviations of these

TABLE V
Atomic coordinates and equivalent isotropic temperature factors (X10^2) for the Pr complex; $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i \cdot a_j$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Pr	0.10523(4)	0.46057(2)	0.16117(3)	3.03(2)
Cl(11)	0.2968(4)	0.3917(2)	−0.0652(3)	9.1(2)
Cl(12)	0.3854(3)	0.3077(2)	0.1029(2)	7.4(1)
Cl(13)	0.1154(3)	0.2777(2)	−0.0938(2)	7.8(1)
C(11)	0.237(1)	0.3474(6)	−0.0111(7)	4.9(4)
C(12)	0.1511(9)	0.4000(5)	0.0006(7)	3.9(4)
O(11)	0.1746(7)	0.3952(4)	0.0796(5)	5.3(3)
O(12)	−0.0647(7)	0.5597(3)	0.0728(5)	5.4(3)
Cl(21)	0.3643(5)	0.6765(3)	0.0458(3)	11.0(2)
Cl(22)	0.352(1)	0.6956(3)	0.1981(5)	19.7(5)
Cl(23)	0.5082(4)	0.5797(5)	0.2120(6)	21.7(6)
C(21)	0.356(1)	0.6307(7)	0.1268(8)	7.1(6)
C(22)	0.218(1)	0.5854(5)	0.0741(7)	4.3(4)
O(21)	0.2190(8)	0.5462(4)	0.1302(6)	5.7(3)
O(22)	−0.1225(7)	0.4059(4)	0.0174(5)	6.0(3)
Cl(31)	−0.1141(4)	0.5153(2)	0.3181(3)	9.1(2)
Cl(32)	−0.089(1)	0.3730(4)	0.3832(7)	18.8(5)
Cl(33)	−0.3207(4)	0.4131(4)	0.1761(6)	19.1(5)
C(31)	−0.142(1)	0.4254(7)	0.279(1)	6.8(6)
C(32)	−0.051(1)	0.4006(5)	0.2517(7)	4.8(4)
O(31)	−0.0013(7)	0.4504(4)	0.2360(5)	4.6(3)
O(32)	−0.0385(9)	0.3349(4)	0.2498(7)	6.7(4)
C(41)	0.4623(9)	0.5018(5)	0.3761(6)	3.8(4)
N(42)	0.3853(8)	0.4446(4)	0.3137(5)	4.1(3)
C(43)	0.457(1)	0.3894(6)	0.3183(8)	5.9(5)
C(44)	0.607(1)	0.3859(8)	0.3832(9)	7.0(6)
C(45)	0.685(1)	0.4428(7)	0.4452(8)	6.5(6)
C(46)	0.615(1)	0.5035(6)	0.4443(7)	5.1(5)
C(47)	0.688(1)	0.5659(7)	0.5070(8)	6.3(6)
C(48)	0.618(1)	0.6220(7)	0.5010(8)	6.2(5)
C(49)	0.462(1)	0.6234(5)	0.4321(7)	4.8(4)
C(50)	0.384(1)	0.6824(6)	0.4215(8)	6.1(5)
C(51)	0.237(1)	0.6793(6)	0.3560(9)	6.5(6)
C(52)	0.168(1)	0.6151(6)	0.3000(8)	5.3(5)
N(53)	0.2385(7)	0.5590(4)	0.3053(5)	3.8(3)
C(54)	0.3853(9)	0.5623(5)	0.3712(6)	3.8(4)
O(51)	0.1280(8)	0.3294(3)	0.2074(6)	5.3(3)
C(56)	0.162(2)	0.2599(7)	0.189(1)	8.8(8)
C(57)	0.041(3)	0.2192(9)	0.108(2)	12.0(10)

atoms from their least-squares plane are significant (−0.16 to 0.15 Å). The large deviations are attributed to differences in Ln–O and Ln–N bond lengths. The angles between the least-squares planes of the square faces of the antiprism are 2.7(2), 2.3(3) and 2.3(2)° for the praseodymium, neodymium and erbium complexes, respectively.

The distances of the lanthanide ions to the two square faces of the square antiprism are substantially different. The distances to the square face formed by the four carboxylate oxygen atoms are 1.231(5), 1.230(5) and 1.170(4) Å and the distances from the lanthanide ion to the other square face are 1.421(5), 1.488(6) and 1.340(4) Å, respectively.

The OH group of the ethanol ligand forms an intramolecular hydrogen bond with the uncoordinated O(32) atom of the monodentate trichloroacetate ligand. The O(32)...O(51) distances are not significantly different in the three complexes, and average 2.63(1) Å.

TABLE VI

Atom coordinates and equivalent isotropic temperature factors $(X10^2)$ for the Nd complex.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Nd	0.10589(5)	0.46132(2)	0.16103(3)	3.93(2)
Cl(11)	0.2967(5)	0.3927(3)	−0.0652(3)	11.2(3)
Cl(12)	0.3862(3)	0.3103(2)	0.1034(2)	9.0(2)
Cl(13)	0.1177(4)	0.2787(2)	−0.0920(3)	9.9(2)
C(11)	0.237(1)	0.3493(6)	−0.0113(7)	6.1(5)
C(12)	0.152(1)	0.4017(5)	0.0002(7)	4.7(4)
O(11)	0.1747(8)	0.3980(4)	0.0787(6)	6.3(4)
O(12)	−0.0650(8)	0.5590(4)	0.0738(5)	6.3(3)
Cl(21)	0.3591(5)	0.6760(3)	0.0429(3)	13.4(3)
Cl(22)	0.359(1)	0.6931(4)	0.1998(6)	24.5(7)
Cl(23)	0.5025(5)	0.5784(6)	0.2055(7)	26.4(8)
C(21)	0.353(1)	0.6304(7)	0.1237(8)	8.2(6)
C(22)	0.216(1)	0.5853(5)	0.0732(7)	5.0(4)
O(21)	0.2166(8)	0.5473(4)	0.1292(6)	6.5(4)
O(22)	−0.1193(8)	0.4069(4)	0.0183(5)	7.0(3)
Cl(31)	−0.1111(5)	0.5142(3)	0.3189(4)	11.2(2)
Cl(32)	−0.082(1)	0.3739(4)	0.3859(7)	20.4(6)
Cl(33)	−0.3167(5)	0.4123(5)	0.1781(7)	21.4(6)
C(31)	−0.139(1)	0.4240(8)	0.280(1)	8.6(7)
C(32)	−0.049(1)	0.4008(6)	0.2532(8)	6.1(5)
O(31)	0.0001(7)	0.4499(4)	0.2357(5)	5.8(3)
O(32)	−0.031(1)	0.3352(5)	0.2524(8)	8.8(5)
C(41)	0.459(1)	0.5027(5)	0.3744(6)	4.8(4)
N(42)	0.3832(8)	0.4460(4)	0.3110(5)	5.1(3)
C(43)	0.457(1)	0.3911(6)	0.3170(8)	6.7(5)
C(44)	0.605(1)	0.3882(8)	0.3814(9)	8.5(7)
C(45)	0.682(1)	0.4440(8)	0.4433(9)	8.1(7)
C(46)	0.613(1)	0.5049(7)	0.4430(7)	6.2(5)
C(47)	0.685(1)	0.5662(8)	0.5046(9)	7.7(6)
C(48)	0.615(1)	0.6218(8)	0.5003(8)	7.5(6)
C(49)	0.460(1)	0.6228(6)	0.4321(7)	6.0(5)
C(50)	0.382(2)	0.6814(7)	0.422(1)	8.0(7)
C(51)	0.235(2)	0.6779(7)	0.3560(9)	8.2(7)
C(52)	0.166(1)	0.6147(6)	0.2999(8)	6.7(5)
N(53)	0.2354(8)	0.5587(4)	0.3036(5)	4.8(3)
C(54)	0.383(1)	0.5626(5)	0.3699(7)	4.8(4)
O(51)	0.131(2)	0.3303(4)	0.206(1)	6.8
C(56)	0.097(1)	0.2697(5)	0.1416(6)	8.8
C(57)	0.163(2)	0.2034(4)	0.192(1)	11.9

TABLE VII
Atom coordinates and equivalent isotropic temperature factors ($\text{X}10^2$) for the Er complex.

Atom	x/a	y/b	z/c	U_{eq}(Å^2)
Er	0.10488(3)	0.46177(2)	0.15925(2)	2.76(2)
Cl(11)	0.3013(3)	0.3977(2)	−0.0663(2)	7.4(1)
Cl(12)	0.3917(2)	0.3168(1)	0.1062(2)	6.4(1)
Cl(13)	0.1223(3)	0.2817(1)	−0.0903(2)	6.6(1)
C(11)	0.2400(8)	0.3533(5)	−0.0111(6)	4.3(4)
C(12)	0.1494(7)	0.4070(4)	−0.0018(6)	3.3(3)
O(11)	0.1736(6)	0.4043(3)	0.0783(4)	4.1(3)
O(12)	−0.0622(6)	0.5550(3)	0.0779(4)	4.3(2)
Cl(21)	0.3503(4)	0.6741(2)	0.0351(2)	9.5(2)
Cl(22)	0.3600(8)	0.6923(3)	0.1992(4)	19.6(4)
Cl(23)	0.5005(4)	0.5734(4)	0.1963(5)	20.5(5)
C(21)	0.349(1)	0.6288(6)	0.1214(7)	6.3(5)
C(22)	0.2105(8)	0.5834(4)	0.0720(6)	3.7(3)
O(21)	0.2142(6)	0.5465(3)	0.1317(4)	4.6(3)
O(22)	−0.1125(6)	0.4104(3)	0.0206(4)	4.9(3)
Cl(31)	−0.1004(3)	0.5146(2)	0.3252(2)	7.3(1)
Cl(32)	−0.0814(6)	0.3712(2)	0.3874(4)	14.4(3)
Cl(33)	−0.3114(3)	0.4141(3)	0.1792(4)	14.5(3)
C(31)	−0.130(1)	0.4248(5)	0.2841(8)	5.7(5)
C(32)	−0.0385(8)	0.4003(4)	0.2562(6)	4.1(4)
O(31)	0.0039(6)	0.4497(3)	0.2329(4)	4.0(2)
O(32)	−0.0174(8)	0.3354(3)	0.2597(6)	6.4(4)
C(41)	0.4501(8)	0.5011(5)	0.3675(5)	3.8(3)
N(42)	0.3720(7)	0.4431(3)	0.3050(5)	3.7(3)
C(43)	0.4446(9)	0.3872(5)	0.3112(6)	4.9(4)
C(44)	0.596(1)	0.3840(6)	0.3766(7)	5.9(5)
C(45)	0.675(1)	0.4415(6)	0.4367(7)	6.1(5)
C(46)	0.6044(9)	0.5024(5)	0.4359(6)	4.8(4)
C(47)	0.677(1)	0.5647(6)	0.4966(7)	5.9(5)
C(48)	0.607(1)	0.6198(6)	0.4932(7)	5.7(5)
C(49)	0.4497(9)	0.6217(5)	0.4249(6)	4.5(4)
C(50)	0.369(1)	0.6795(6)	0.4154(8)	6.2(5)
C(51)	0.223(1)	0.6745(6)	0.3512(8)	6.3(5)
C(52)	0.1527(9)	0.6114(5)	0.2939(6)	4.7(4)
N(53)	0.2252(6)	0.5566(3)	0.2972(5)	3.6(3)
C(54)	0.3724(8)	0.5607(4)	0.3629(6)	3.8(3)
O(51)	0.1269(6)	0.3351(3)	0.1966(5)	4.3(3)
C(56)	0.088(2)	0.2729(6)	0.132(1)	8.8(7)
C(57)	0.156(2)	0.2070(7)	0.185(1)	12.(1)

The correlation of the Ln–L bond lengths with the atomic number of the lanthanide atom, as shown in Figure 3, is consistent with the lanthanide contraction caused by the shielding by the *f* electrons.[20] Figure 3 also contains data for the isostructural complex of Sm, which has recently been determined.[21]

TABLE VIII
Selected structural parameters for the lanthanide complexes.

	Pr complex	Nd complex	Er complex
Bond lengths (Å) and bond angles (°) around the central ion			
Ln-O(11)	2.440(6)	2.425(7)	2.321(8)
Ln-O(12)	2.420(6)	2.410(7)	2.308(5)
Ln-O(21)	2.413(6)	2.400(7)	2.302(8)
Ln-O(22)	2.433(6)	2.419(7)	2.312(5)
Ln-O(31)	2.427(6)	2.413(7)	2.303(9)
Ln-N(42)	2.642(7)	2.619(7)	2.509(5)
Ln-N(53)	2.635(7)	2.614(7)	2.525(6)
Ln-O(51)	2.509(6)	2.506(8)	2.396(6)
O(11)-Ln-O(21)	72.3(2)	72.2(3)	72.1(3)
O(11)-Ln-O(22)	78.3(3)	78.0(3)	78.3(2)
O(12)-Ln-O(21)	75.5(3)	75.4(3)	76.2(2)
O(12)-Ln-O(22)	74.3(2)	74.1(3)	73.8(2)
O(31)-Ln-N(53)	75.0(2)	74.8(2)	73.9(3)
O(31)-Ln-O(51)	74.4(2)	74.7(5)	76.0(3)
N(42)-Ln-N(53)	62.2(2)	62.7(2)	64.9(2)
N(42)-Ln-O(51)	76.9(2)	76.7(5)	75.6(2)
O(11)-Ln-N(42)	79.0(2)	79.1(2)	79.0(2)
O(11)-Ln-O(51)	73.2(2)	72.9(5)	72.5(3)
O(12)-Ln-O(31)	81.6(2)	81.5(3)	80.6(3)
O(12)-Ln-N(53)	79.8(2)	79.6(2)	78.1(2)
O(21)-Ln-N(42)	74.6(2)	74.9(3)	76.3(2)
O(21)-Ln-N(53)	71.7(2)	72.0(2)	71.1(3)
O(22)-Ln-O(31)	82.2(2)	82.4(3)	83.1(3)
O(22)-Ln-O(51)	75.1(2)	75.2(5)	74.4(2)
Ln-O(11)-C(12)	137.0(6)	138.4(6)	139.9(5)
Ln-O(12)-C(12)	154.8(6)	153.7(7)	150.6(8)
Ln-O(21)-C(22)	151.9(7)	152.0(7)	148.9(4)
Ln-O(22)-C(22)	139.4(6)	140.4(7)	142.3(7)
Ln-O(31)-C(32)	136.1(6)	137.6(7)	138.2(7)
Ln-N(42)-C(41)	118.8(5)	118.8(6)	117.4(5)
Ln-N(42)-C(43)	121.6(6)	122.5(6)	123.0(5)
Ln-N(53)-C(52)	120.9(6)	122.0(6)	122.6(4)
Ln-N(53)-C(54)	118.7(5)	118.6(6)	117.5(6)
Ln-O(51)-C(56)	139.9(7)	125.8(10)	129.9(8)
Contact distances of ligands atoms around the lanthanide ions			
O(11)···O(21)	2.86(1)	2.84(1)	2.720(8)
O(11)···O(22)	3.08(1)	3.05(2)	2.93(1)
O(12)···O(21)	2.96(1)	2.94(2)	2.85(1)
O(12)···O(22)	2.93(1)	2.91(1)	2.775(8)
O(31)···O(51)	2.98(1)	2.99(3)	2.89(1)
O(31)···N(53)	3.09(1)	3.06(1)	2.906(9)
O(51)···N(42)	3.20(1)	3.18(2)	3.007(8)
N(42)···N(53)	2.73(1)	2.72(1)	2.70(1)
O(32)···O(51)	2.63(2)	2.63(4)	2.62(2)

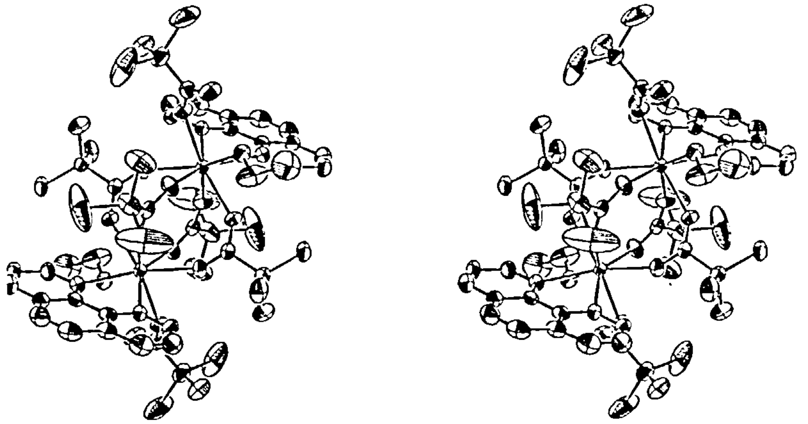

FIGURE 1 Stereoscopic view of the erbium complex dimer.

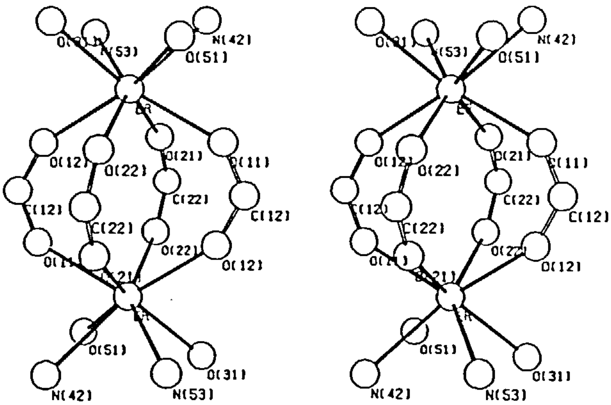

FIGURE 2 Atomic numbering scheme of the central fragment of the complex dimers.

DISCUSSION

The Eu–N bond lengths for the tris(acetylacetonato)(1,10-phenanthroline)Eu(III) complex are 2.64(1) Å,[11] which is approximately 0.05 Å larger than would be expected from the plot of Ln–N bond distances given in Figure 3. However, if the average Ln–O distances to oxygen atoms belonging to bidentate ligands are compared for the Pr, Nd, Eu and Er complexes, we find 2.426(6), 2.413(6), 2.378(8) and 2.311(4) Å respectively, not inconsistent with expectations based on the lanthanide contraction. There is no apparent explanation for the longer Eu–N bond lengths in the tris(acetylacetonato)(1,10-phenanthroline) Eu(III) complex.

The contact distances between ligand atoms around the lanthanide ions are given in Table VIII. The contact distances decrease as the atomic number of the lanthanide atom increases. The contact distances are substantially larger than the sum of the van der Waals radii of the corresponding atoms, even in the heavier lanthanide complex.

However, the sizes of the phenanthroline, ethanol and trichloroacetate ligands are sufficiently large to prevent any small ligand, such as water, from coordinating to the central ion. Therefore, the coordination of the light lanthanide ions in these complexes is the same as that of the heavy lanthanides.

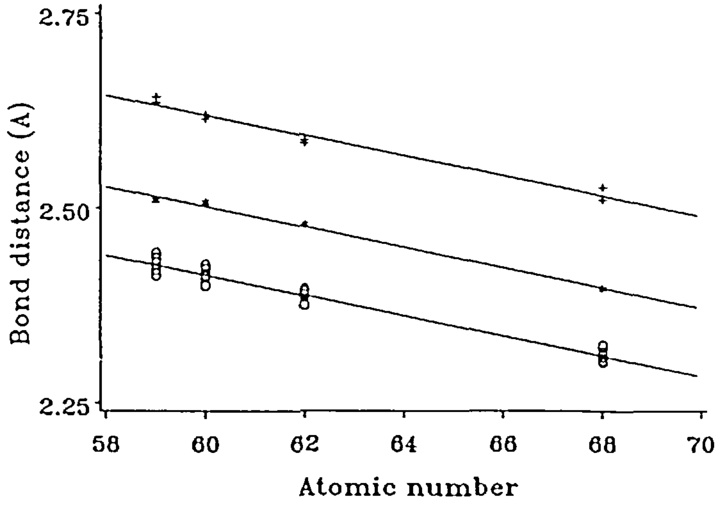

FIGURE 3 Correlation of Ln-ligand bond lengths (Å) and atomic number; o: Ln-O (trichloroacetate); *: Ln-O (ethanol); +: Ln-N (phenanthroline).

For an undistorted square antiprism, with identical ligands, the angle α between the $\bar{8}$ axis of the square antiprism and an Ln-L bond is 59.26° for a structure with minimum repulsion energy based on the hard sphere model.[22] The values for O(11), O(12), O(21) and O(22) (Table IX) are close to the ideal value. However, the value for O(51) is greater and that for O(31) is smaller. This may be due to the effect of intermolecular interactions.

TABLE IX
Structural parameter (α)* of the square antiprismatic configuration of the complexes.

α	Pr complex	Nd complex	Er complex
O(11)	59.8(2)	59.7(2)	59.8(2)
O(12)	59.5(2)	59.5(2)	59.6(2)
O(21)	59.2(2)	59.0(2)	59.3(2)
O(22)	59.5(2)	59.3(2)	59.5(2)
O(31)	49.7(2)	49.8(2)	49.5(2)
N(42)	55.5(2)	55.4(2)	54.2(2)
N(53)	58.6(2)	58.7(2)	60.2(2)
O(51)	61.3(2)	61.5(2)	62.3(2)

* See text for explanation.

In the central fragment of the dimer, the eight carboxyl oxygen atoms of the four bridging bidentate trichloroacetate form a skewed square prism (see Figure 2), which is similar to that found in the structure of trifluoroacetate lanthanide complexes.[12,14]

The skewness of a square prism may be measured by the angle, ε, between the Ln–Ln vector and the normal to a square face of the square prism. The values of ε for the Pr complex, Nd complex, Er complex and the trifluoroacetate praseodymium complex[12] are 4.8(6), 4.2(6), 2.8(5) and 15.1(5)°, respectively. The skewed square prism corresponds to a more compact molecular packing than does an undistorted square prism. The F atoms in the trifluoroacetate praseodymium complex are smaller compared to the Cl atoms in the complexes discussed here, allowing a greater degree of skewness. The heavier lanthanide complexes are more compact, which limits the degree of skewness of the square prism. However, the skewed square prism structure does not significantly change the values of associated ligands from ideal ones. These observations confirm that the skewed nature of the structure is related to the need to achieve a compact central portion of the dimer rather than to the bond angle requirements of the lanthanide ions.[12]

The O–C–O angles for the bridging bidentate trichloroacetate ligands averaged over the three structures is 128.9°. Assuming this value and an undistorted square prism with $\alpha = 59.26°$, the Ln–O–C angles would be 146.3°. However, the individual values of the Ln–O–C angles in these complexes are substantially different, although the average value of two Ln–O–C angles for each bidentate trichloroacetate ligand is approximately 146°.

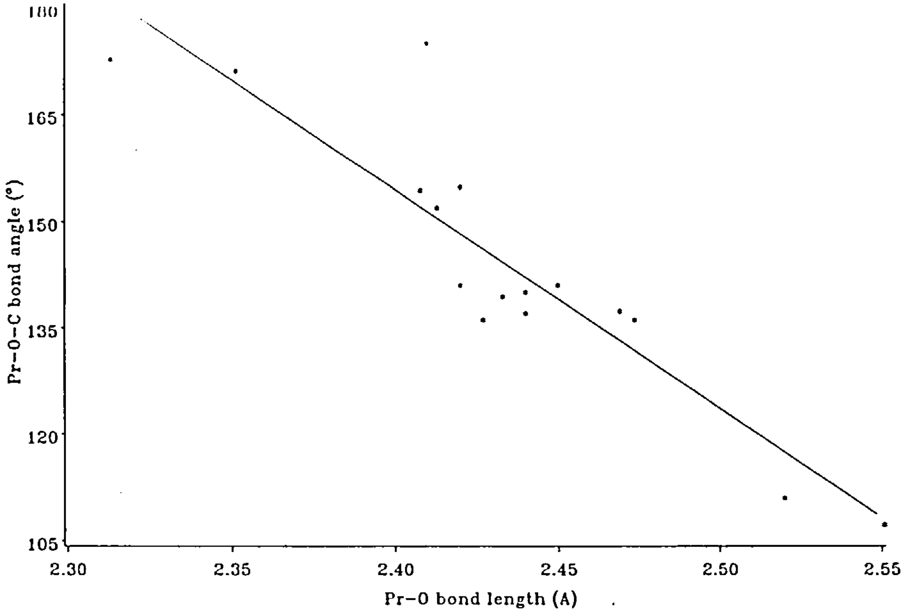

FIGURE 4 Correlation between Pr-O-C bond angles and Pr-O bond lengths.

The large variations in the individual Ln–O–C angles from their ideal value are clearly a result of the skewed square prism structure. This suggests that the compactness of the structure is more important than the orientation of the carboxylate O atom coordinated to the lanthanide ion. However, the orientation of the carboxylate O atom does affect the bonding of the O atom to the lanthanide ion to a limited extent. This is demonstrated by the correlation between Pr–O bond lengths and Pr–O–C angles from the trichloroacetate and trifluoroacetate[12,14] praseodymium complexes. Figure 4 indicates that the Pr–O bond length decreases as the Pr–O–C angle expands.

Calculations[23] based on a similar complex, $[(CCl_3COO^-)(phen)(C_2H_5OH)Gd^{3+}]_2$, by the INDO method[24] showed that the bonds between the central ion and the ligand atoms are contributed mainly by the $4d$,$6s$ orbitals. These complexes are expected to show similar results. The lone-pair electrons of the O and N atoms fill the d^4sp^3 hybrid orbitals of each central Ln^{3+} atom. The aforementioned calculation also indicated that the bonds between the carboxylate O atoms and the Gd^{3+} are approximately 50% ionic in character. This is consistent with the observed small effect of the Ln–O–C angles on the Ln–O bond length

In the trichloroacetate ligands, the C–O bond lengths for both the bridging bidentate ligands and the monodentate ligands are the same and their average value is 1.23(1) Å. The C–C and C–Cl bond lengths of all the trichloroacetate ligands are also similar, with average values 1.55(1) and 1.74(2) Å, respectively. The large and highly anisotropic temperature factors of the chlorine atoms indicate that the librations of the CCl_3 group around the C–C bond are relatively large. A similar phenomenon was observed in the trifluoroacetate lanthanide complex.[12]

The two nitrogen atoms of the phenanthroline ligands are chelated to the lanthanide ion with a normalized bite[23] of 1.03, 1.04 and 1.07 Å for the praseodymium, neodymium and erbium complexes, respectively. In each case, the atoms of the phenanthroline group do not deviate significantly from their least-squares plane. However, the lanthanide ion is significantly removed from that least-squares plane. The molecular structures of the phenanthroline ligands in each lanthanide complex are identical and similar to the structure of phenanthroline in ammonium picrate 1,10-phenanthroline.[25] The phenanthroline ligands possess local C_{2v} symmetry.

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