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Structure of a Gadolinium Hexaaza Macrocycle Complex with a $Gd_2(OAc)_8$ Counterion

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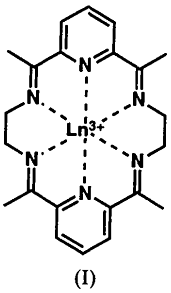
Abstract. Di[bis(acetato-*O*,*O*′){2,7,13,18-tetramethyl-3,6,14,17,23,24-hexaazatricyclo[17.3.1.$1^{8,12}$]tetracosa-1(23),2,6,8,10,12(24),13,17,19,21-decaene-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*⁗′}gadolinium(III)] bis[(μ-acetato-*O*:*O*,*O*′)-(μ-acetato-*O*:*O*′)-bis(acetato-*O*,*O*′)-gadolinium(III)] chloroform benzene solvate, $2[Gd(C_{22}H_{26}N_6)(C_2H_3O_2)_2][Gd_2(C_2H_3O_2)_8].C_6H_6.4CHCl_3$, $M_r = 2642.1$, triclinic, $P\bar{1}$, $a = 12.488\,(2)$, $b = 14.198\,(3)$, $c = 16.848\,(3)$ Å, $\alpha = 66.65\,(3)$, $\beta = 69.65\,(3)$, $\gamma = 86.66\,(3)°$, $V = 2560.4\,(8)$ Å^3, $Z = 1$, $D_x = 1.714$ Mg m^{-3}, $\mu = 2.96$ mm^{-1}, λ(Mo $K\alpha$) = 0.71069 Å, $F(000) = 1302$, $T = 298$ K, $R = 0.041$, $wR = 0.037$ for 3956 observed reflections. The structure consists of two inversion-related monocationic bis(acetato) gadolinium macrocycle complexes and a centrosymmetric dianionic gadolinium acetate dimer. In the cation each Gd ion is coordinated by six N atoms from the macrocycle and two bidentate acetate anions, coordinated on opposite sides of the Gd. The dianion is composed of a centrosymmetric dimer in which each Gd is coordinated by five O atoms from four bridging acetates (two of which are unique) and two bidentate terminal acetates.

Introduction. The condensation of diacetylpyridine and ethylenediamine in the presence of a lanthanide template ion results in a hexaaza macrocyclic complex (I) (Backer-Dirks, Gray, Hart, Hursthouse & Schoop, 1979; Bombierie, Benetollo, Polo, De Cola, Smailes & Vallarino, 1986; De Cola, Smailes & Vallarino, 1986; Arif, Backer-Dirks, Gray, Hart & Hursthouse, 1987; Cabral, Cabral, Cummins, Drew, Rodgers & Nelson, 1978). As we have reported previously, the Gd complexes are of particular interest because of their potential as magnetic resonance imaging contrast agents (Smith, Brainard, Morris, Jarvinen & Ryan, 1989). The title compound was obtained as a by-product of the preparation of the complex reported previously (Smith *et al.*, 1989).



(I)

Experimental. The Gd macrocycle complex was prepared according to Smith *et al.* (1989). The crude product was recrystallized from chloroform/benzene. The title compound is a minor product owing to incomplete reaction of the starting materials. A colorless crystal of approximate dimensions 0.2 × 0.06 × 0.1 mm was used for data collection on a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were refined by least-squares fit of 25 reflections in the range $13.6 < \theta < 14.3°$. Intensity data were measured by the $\theta/2\theta$ scan technique to maximum $2\theta = 45°$. Two standard reflections ($1\bar{8}2$, $4\bar{6}\bar{7}$), monitored every 7200 s, showed 12.9% decay. An orientation matrix was checked every 200 reflections. 6968 reflections were collected ($2 \leq 2\theta \leq 45°$; $0 \leq h \leq 13$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$), of which 5699 were unique, $R_{\rm int} = 0.025$, with 3956 judged significant [$F > 4.0\sigma(F)$]. $\sigma(F_o)$ was based on counting statistics. 13.3% decay was corrected linearly. An empirical absorption correction was applied using ψ scans of two equivalent reflections at $\theta = 9.9°$ (correction factors in the range 0.955–1.00, average transmission factor 96.56%). Lp corrections were applied. Metal positions were determined from a Patterson function, other non-H atoms from difference Fourier syntheses. Anisotropic full-matrix least-squares refinement was based on F with 587 refined parameters and a weighting scheme $w^{-1} = \sigma^2(F) + 0.0001F^2$. $R = 0.041$, $wR = 0.037$; $S = 1.59$; $(\Delta/\sigma)_{\rm max} = 1.26$, $(\Delta/\sigma)_{\rm av} = 0.041$; final $-1.04 < \Delta\rho < 0.81$ e Å^{-3}; secondary extinction $\chi = 0.00005\,(2)$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$. H atoms were located in a difference map and calculated using the riding model with fixed isotropic U values. Cal-

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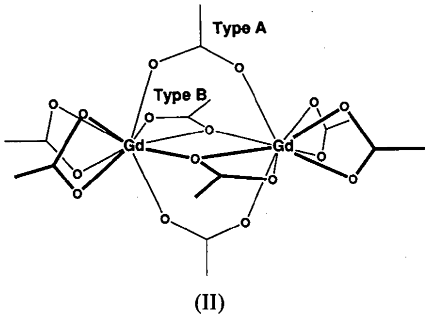
culations were performed using *SHELXTL-Plus* (Sheldrick, 1990) on a VAX station 3100. Scattering factors were supplied with *SHELXTL-Plus*.

Discussion. Final atomic coordinates for the non-H atoms are listed in Table 1.* The bond distances and angles for the Gd macrocycle complex are very similar to those previously reported (Smith *et al.*, 1989), and the labelling scheme is the same. The Gd ion is ten-coordinate with six N atoms from the macrocycle and four O atoms from two bidentate acetate anions bound to the metal. The acetate ions are coordinated on opposite sides of the metal ion, and the dihedral angle between the planes of the two Gd(OAc) fragments is 97.1° [compared to 95.1° in Smith *et al.* (1989)]. The macrocycle is composed of two approximately planar halves as described previously (Arif *et al.*, 1987). The least-squares plane which includes N1 is described by the equation $11.998x + 3.425y + 9.789z = 3.4849$ (fractional coordinates) and the average deviation from this plane is 0.0788 Å. The plane which includes N4 is described by the equation $9.545x + 0.764y - 4.789z = -0.6084$ and has an average deviation of 0.0578 Å. The angle between the normals to these planes is 52.9° [compared to 47.9° in Smith *et al.* (1989)]. The only two torsion angles which are considerably larger than 0° are those around the ethylenediamine linkages (N2—C3—C4—N3 = 54.2 and N5—C15—C16—N6 = 54.8°). These values are similar to those found previously [54.3 and 57.0° in Smith *et al.* (1989)].



(II)

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$)

Equivalent isotropic U's are defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Gd1	1006 (1)	2650 (1)	2277 (1)	33 (1)
Gd2	3910 (1)	3873 (1)	6068 (1)	33 (1)
Cl1	2355 (3)	215 (3)	7754 (3)	85 (2)
Cl2	806 (5)	−878 (3)	9600 (3)	129 (3)
Cl3	2986 (4)	−1593 (3)	8958 (4)	146 (4)
Cl4	3447 (4)	5987 (4)	1500 (3)	121 (3)
Cl5	2457 (5)	7522 (6)	2137 (6)	215 (7)
Cl6	4444 (7)	8058 (5)	480 (5)	218 (6)
O1	−948 (7)	2206 (6)	3432 (6)	53 (5)
O2	−793 (6)	2286 (6)	2081 (6)	51 (4)
O3	2993 (7)	2231 (7)	1955 (6)	63 (5)
O4	2720 (7)	3837 (7)	1687 (6)	57 (5)
O5	2189 (7)	2822 (7)	6408 (6)	62 (5)
O6	2203 (6)	3225 (6)	7528 (5)	48 (4)
O7	4126 (7)	5691 (6)	4773 (5)	43 (4)
O8	2425 (7)	5068 (6)	5825 (6)	71 (5)
O9	4460 (8)	2119 (6)	6487 (6)	63 (5)
O10	4696 (7)	2827 (7)	7348 (5)	58 (5)
O11	4177 (7)	3742 (6)	4662 (5)	52 (4)
O12	4412 (7)	5126 (6)	6521 (5)	48 (4)
N1	1556 (7)	3649 (7)	499 (6)	35 (5)
N2	321 (8)	4433 (7)	1663 (6)	36 (5)
N3	725 (8)	3751 (7)	3269 (6)	40 (5)
N4	1300 (7)	1834 (7)	3852 (6)	41 (5)
N5	866 (8)	672 (7)	3090 (6)	42 (5)
N6	1583 (9)	1630 (7)	1190 (7)	48 (6)
C1	1484 (9)	4664 (9)	141 (8)	43 (6)
C2	752 (10)	5072 (9)	836 (9)	45 (7)
C3	626 (11)	6224 (8)	476 (8)	66 (7)
C4	−397 (10)	4752 (9)	2392 (8)	46 (6)
C5	301 (10)	4754 (9)	2956 (8)	52 (7)
C6	1113 (10)	3493 (10)	3921 (8)	51 (7)
C7	1248 (12)	4178 (11)	4380 (9)	87 (10)
C8	1420 (9)	2408 (9)	4292 (8)	44 (6)
C9	1739 (11)	2018 (11)	5067 (8)	60 (8)
C10	1888 (12)	972 (13)	5397 (9)	77 (9)
C11	1719 (11)	392 (10)	4977 (9)	68 (8)
C12	1454 (9)	827 (9)	4207 (8)	43 (6)
C13	1229 (10)	221 (9)	3728 (8)	42 (6)
C14	1481 (11)	−890 (8)	4085 (9)	72 (8)
C15	608 (12)	139 (9)	2583 (9)	67 (8)
C16	1513 (12)	510 (9)	1637 (8)	64 (8)
C17	2075 (10)	2085 (11)	317 (9)	52 (7)
C18	2566 (12)	1557 (10)	−340 (9)	81 (9)
C19	2131 (9)	3226 (9)	−111 (8)	42 (7)
C20	2699 (10)	3817 (11)	−1040 (8)	54 (7)
C21	2613 (11)	4871 (11)	−1375 (9)	65 (8)
C22	2010 (10)	5290 (10)	−770 (8)	55 (7)
C23	−1385 (11)	2201 (8)	2868 (9)	43 (7)
C24	−2663 (10)	2113 (11)	3155 (9)	81 (9)
C25	3392 (11)	3158 (13)	1626 (9)	52 (8)
C26	4657 (11)	3460 (12)	1158 (10)	90 (10)
C27	1691 (10)	2826 (8)	7192 (8)	40 (6)
C28	498 (10)	2352 (9)	7745 (9)	68 (8)
C29	3076 (13)	5800 (10)	5139 (10)	56 (8)
C30	2613 (11)	6796 (10)	4759 (9)	103 (9)
C31	4724 (10)	2099 (9)	7127 (9)	44 (7)
C32	5129 (11)	1104 (9)	7694 (9)	77 (9)
C33	4778 (11)	4174 (10)	3824 (8)	42 (7)
C34	4563 (11)	3802 (10)	3174 (8)	80 (9)
C35	1866 (11)	−998 (9)	8661 (8)	60 (7)
C36	3712 (14)	7117 (13)	1595 (11)	109 (12)
C37	5297 (40)	9087 (43)	4920 (34)	244 (39)
C38	4976 (38)	9687 (35)	4385 (38)	276 (47)
C39	4663 (18)	10639 (27)	4324 (18)	184 (22)

The bond distances and angles for the centrosymmetric Gd acetate dimer (II) are listed in Table 2, and the labelling diagram is presented in Fig. 1. Each Gd atom is coordinated by five O atoms from four bridging acetates (two of which are unique, illustrated as types *A* and *B*), and two bidentate terminal acetates. One type of bridging acetate (type *A*) is bound *via* one O atom to each Gd atom and is approximately symmetric with respect to the two Gd atoms. The other type of bridging acetate (type *B*) is bound *via* both O atoms to one Gd atom and shares one O atom with the other Gd atom. The Gd—O distances range from 2.339 (7) Å for Gd2—O7*A* to 2.589 (7) Å for Gd2—O7. The latter two distances are both for the type *B* bridging O atom with the two

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* Lists of all bond distances, bond angles, structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55351 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0610]

Table 2. *Bond lengths* (Å) *and angles* (°) *for the gadolinum acetate dimer*

Gd2—O5	2.453 (10)	O8—C29	1.253 (13)
Gd2—O6	2.495 (6)	O9—C31	1.222 (20)
Gd2—O7	2.589 (7)	O10—C31	1.225 (19)
Gd2—O8	2.470 (9)	O11—C33	1.250 (12)
Gd2—O9	2.432 (8)	O12—C33*A*	1.264 (15)
Gd2—O10	2.566 (9)	C27—C28	1.482 (15)
Gd2—O11	2.357 (9)	C29—C30	1.480 (19)
Gd2—O12	2.383 (10)	C31—C32	1.533 (17)
Gd2—Gd2*A*	3.960 (1)	C33—C34	1.493 (24)
Gd2—O7*A*	2.339 (7)	C37—C38	1.141 (74)
O5—C27	1.252 (16)	C37—C39*A*	1.489 (79)
O6—C27	1.265 (19)	C38—C39	1.358 (63)
O7—C29	1.270 (16)		

O5—Gd2—O6	52.4 (3)	O7—Gd2—O12	70.5 (3)
O5—Gd2—O7	112.9 (3)	O8—Gd2—O12	79.7 (3)
O6—Gd2—O7	122.7 (2)	O9—Gd2—O12	125.9 (3)
O5—Gd2—O8	73.4 (3)	O10—Gd2—O12	76.1 (3)
O6—Gd2—O8	73.1 (2)	O11—Gd2—O12	136.2 (2)
O7—Gd2—O8	51.2 (2)	Gd2—O5—C27	94.6 (9)
O5—Gd2—O9	75.2 (3)	Gd2—O6—C27	92.2 (6)
O6—Gd2—O9	88.0 (3)	Gd2—O7—C29	90.9 (6)
O7—Gd2—O9	147.3 (3)	Gd2—O8—C29	97.0 (8)
O8—Gd2—O9	148.6 (3)	Gd2—O9—C31	95.3 (8)
O5—Gd2—O10	104.6 (3)	Gd2—O10—C31	88.8 (8)
O6—Gd2—O10	74.4 (3)	Gd2—O11—C33	139.2 (10)
O7—Gd2—O10	141.5 (3)	O5—C27—O6	120.5 (10)
O8—Gd2—O10	139.3 (3)	O5—C27—C28	120.5 (14)
O9—Gd2—O10	51.3 (4)	O6—C27—C28	119.0 (12)
O5—Gd2—O11	76.0 (3)	O7—C29—O8	120.5 (12)
O6—Gd2—O11	128.2 (3)	O7—C29—C30	120.1 (9)
O7—Gd2—O11	70.0 (3)	O8—C29—C30	119.4 (12)
O8—Gd2—O11	89.9 (3)	O9—C31—O10	124.5 (11)
O9—Gd2—O11	82.3 (3)	O9—C31—C32	118.5 (13)
O10—Gd2—O11	129.8 (3)	O10—C31—C32	116.9 (14)
O5—Gd2—O12	137.9 (3)	O11—C33—C34	117.5 (11)
O6—Gd2—O12	89.3 (3)		

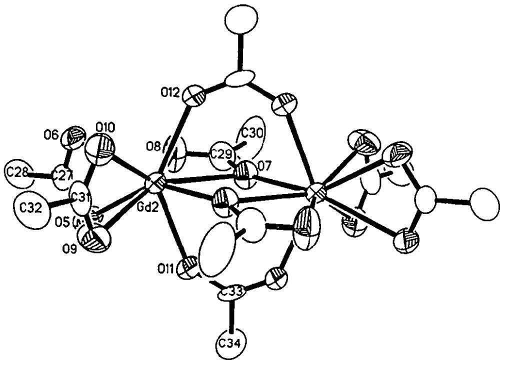

Fig. 1. Labelling diagram for the gadolinium acetate dimer [$Gd_2(C_2H_3O_2)_8$] with 50% probability thermal ellipsoids.

Table 3. *Carboxylate bridged dimers found in the Cambridge Structural Database*

Metal	Ligand	Ln···Ln distance (Å)	Reference
Nd	Fluoroacetate	4.026	Aslanov, Ionov & Kiekbaev (1976)
Nd	Glycinate	4.127	Pakhomov, Bukov & Panyushkin (1982)
Nd	Methylthioacetate	4.066	Kondo, Shimoi, Ouchi & Takeuchi (1982)
Nd	Acetate	4.149	Kirillova, Gusev, Furmanova, Soboleva & Edgorbekov (1983)
Nd	Glycinate	4.218	Legendziewicz *et al.* (1984)
Nd	1-Hydroxy-2-naphthoate	4.087	Ohki, Suzuki, Takeuchi, Shimoi & Ouchi (1986)
La	Chloroacetate	4.142	Imai, Shimoi & Ouchi (1987)
Nd	Chloroacetate	4.060	Imai *et al.* (1987)
Eu	Chloroacetate	3.974	Imai *et al.* (1987)
Eu	3,4-Furandicarboxylate	4.000	Zhibang, Ninghai, Zhongsheng & Jiazan (1988)
Tb	3,4-Furandicarboxylate	3.956	Zhibang *et al.* (1988)
Ho	L-Glutamate	3.897	Csoregh *et al.* (1989)
Dy	L-Glutamate	3.909	Csoregh *et al.* (1989)

Gd atoms. The average Gd—O distance is 2.454 Å, and the Gd···Gd distance is 3.960 (1) Å.

A search of the Cambridge Structural Database [version 4.5 (Allen *et al.*, 1979; Allen, Kennard & Taylor, 1983)] using the bridging portion of the molecule revealed 13 lanthanide compounds which display the same arrangement of four bridging acetates. The Gd···Gd distance reported in this paper is among the shortest known for lanthanide clusters of this type. The shortest Ln···Ln distances found were 3.897 and 3.909 Å for an Ho and a Dy (Csoregh, Czugler, Kierkegaard, Legendziewicz & Huskowska, 1989) L-glutamate complex. The longest distance found was 4.218 Å for a Nd glycinate complex (Legendziewicz, Huskowska, Waskowska & Argay, 1984) and the average of all 13 is 4.047 Å. The Ln···Ln distances for each of these dimers are listed in Table 3 along with the metal, ligand type and reference.

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Structure of [Bis(2-diphenylphosphinoethyl)phenylphosphine-*P*,*P*,*P*]carbonyl(phenylthiolato)cobalt(I), $[Co\{Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}(SPh)(CO)]$

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Abstract. $[Co(C_{34}H_{33}P_3)(C_6H_5S)(CO)]$, $M_r = 730.68$, monoclinic, $P2_1$, $a = 11.163$ (2), $b = 15.499$ (3), $c = 10.427$ (2) Å, $\beta = 94.18$ (3)°, $V = 1799.34$ (93) Å^3, $Z = 2$, $D_x = 1.349$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 6.928$ cm^{-1}, $F(000) = 760$, $T = 296$ K, final $R = 0.043$ for 1866 observed unique reflections. The compound is an asymmetric molecule with a five-coordinate Co atom. The Co—S, Co—C and average value of Co—P bond distances are 2.302 (3), 1.741 (9) and 2.160 (3) Å, respectively.

Introduction. Transition-metal complexes containing phosphino ligands have been studied extensively, not only because of their facile electron-transfer properties and variation of molecular structure but also owing to their potential application as homogeneous or heterogeneous catalysts. Metal thiolato complexes are known as ubiquitous biological electron-transfer mediators (Blower & Dilworth, 1987). Yet complexes blending both poly-phosphino and thiolato ligands have received relatively little attention and only a few reports have been found in this realm (Canich, Cotton, Dunbar & Falvello, 1988), and the structures of complexes blending poly-phosphino, carbonyl and thiolato ligands have not been seen up to now.

In a programme aimed at understanding the synergetic effect between atoms or groups within a molecule, we have explored the coordination chemistry and the reactivity of metal complexes with both thiolato and ditertiary phosphino ligands (Wei, Liu, Huang, Hong, Huang & Kang, 1991). Herein, we report the synthesis and crystal structure of a cobalt complex blending poly-phosphino, thiolato and carbonyl ligands, [Co(dppep)(SPh)(CO)] [dppep = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$].

Experimental. [Co(dppep)(SPh)(CO)] was prepared by the reaction of $CoCl_2.6H_2O$, dppep, NaSPh and $Mo(CO)_6$ in MeCN at room temperature, and crystals suitable for X-ray analysis were grown by keeping the reaction solution at 263 K. Diffraction intensities were collected from a red plate crystal of 0.30 × 0.30 × 0.15 mm on an Enraf–Nonius CAD-4 diffractometer in the ω–2θ-scan mode [scan rate 1–7° min^{-1} (in ω); scan width $(0.90 + 0.350\tan\theta)$°] using graphite-monochromated Mo $K\alpha$ radiation. Cell constants were obtained from least-squares refinement of 25 reflections, using a setting of θ angles from 12 to 18°. Systematic absences: $0k0$, $k = 2n$. A total of 3488 reflections were collected in the range of $2 < 2\theta < 50°$ ($0 \le h \le 13$, $0 \le k \le 18$, $-12 \le l \le 12$). The intensities were monitored by three representative reflections. The data were corrected for the fluctuation of the monitored reflections (between 1.000 and 1.039), the Lp factor, and empirical absorption (*DIFABS*; Walker & Stuart, 1983) (between 1.371 and 0.840), but no extinction correction was made. Of 3134 unique reflections, 1866 with $I > 3\sigma(I)$ were used for structure solution and

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