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Eight-Coordination. Synthesis and Structure of the Schiff-Base Chelate Bis(N,N'-disalicylidene-1,2-phenylenediamino)Cerium(IV)

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In an effort to elucidate the factors that determine the geometry of eight-coordinate complexes we synthesized and structurally characterized the complex bis(N,N'-disalicylidene-1,2-phenylenediamino)-Cerium(IV), Ce(salophen)$_2$. It is a square antiprismatic species with each chelating ligand spanning sss edges. The Ce–O bonds average 2.214 Å, appreciably shorter than the Ce–N distance of 2.606 Å. The two ligands have the sandwich orientation and the trapezoidal planes intersect at 88.2°. The δ angles are 7.0°, 2.6°, 56.5° and 55.9° and the φ angles are 30.0° and 28.6°. The complex crystallized in space group $P2_1/C$ with $Z = 4$, $a = 11.090(2)$ Å, $b = 16.332(3)$ Å, $c = 18.916(3)$ Å, $\beta = 70.10(2)°$ and $d_{calc} = 1.585$ g/cm^3.

Introduction

The stereochemistry of eight-coordination has become better understood as additional structures are characterized, following the early discussions of possible coordination polyhedra [2–6] and work on the minimization of the repulsion energy and the construction of potential energy surfaces using appropriate values for bond lengths and bites of chelating ligands [7]. The stereochemistry of eight-coordinate compounds is usually discussed in relation to one of three limiting polyhedra: the square antiprism (SAP), the dodecahedron (DOD) and the bicapped trigonal prism (BCTP) which are related by simple stretching of one or two edges in a reaction cycle [4, 5] of the form

$$\begin{tikzcd} & \mathrm{DOD} \arrow[dl, shift left] \arrow[dr, shift left] & \\ \mathrm{SAP} \arrow[ur, shift left] \arrow[rr, shift left] & & \mathrm{BCTP} \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd}$$

Several criteria have been put forth [2–6] to describe real molecules along the reaction path, but it seems that the most powerful and simple one is the dihedral angle criterion [4–6].

A stereochemical rule regarding geometry in eight-coordinate complexes was formulated by Orgel in 1960 [8]. He suggested that systems of the type MX_4Y_4 ($M = d^1$ or d^2 metal ion, $X = \pi$-nonbonding or π-donor, and $Y = \pi$-acceptor) should adopt a dodecahedral geometry with X and Y sorting into A and B sites [2] respectively since the occupied metal $d_{x^2-y^2}$ orbital can π-bond with the π-acceptor ligands in the B sites. Later, it was pointed out [9] that for d^0 ions the π-donor ligands should occupy the B sites so that the π-donor ligands can π-backbond with the empty metal $d_{x^2-y^2}$ orbital. This rule has proved quite successful in predicting geometries, although as Orgel himself emphasized the 'energy balance' between SAP and DOD geometries is a 'delicate' one and other factors such as crystal packing can overpower the electronic factor. In the case of $M(XY)_4$ systems (XY = bidentate ligand) however, there are many reports of complexes where the X and Y atoms do not sort into the A and B sites according to Orgel's rule [10, 11]. This is of course to be expected since the bidentate ligand bite imposes severe restrictions on which DOD and SAP edges can and cannot be spanned by the ligand.

In the present case of $M(XYYX)_2$ systems (XYYX = quadridentate ligand) the steric restrictions imposed by the ligand are even more severe and Orgel's rule must be used with caution, along with other probably more important factors in predicting or rationalizing structural results. In this report we present our results on the structure of such a complex, $M(XYYX)_2$ where $M = Ce^{4+}$ and XYYX is the Schiff base N,N'-disalicylidene-1,2-phenylenediamine(2–)(salophen) and compare them to the structure of similar complexes in order to elucidate the factors that determine the geometry of the complex.

Experimental

Synthesis

A solution of ceric ammonium nitrate (2 mmol) in dimethylformamide (DMF) was added dropwise and with stirring to a boiling solution of H_2salophen (4.2 mmol) in DMF (the swift addition of the ceric salt to the ligand solution produced the non-ionized Schiff base complex of Ce(IV) which dissolved with

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difficulty). The yellow solution turned dark red immediately. When the addition was complete the mixture was removed from the hot plate and dry ammonia gas was passed through the vigorously-stirred solution for 30 min. On cooling overnight a dark red precipitate was formed. This was filtered, washed with ethanol and recrystallized from DMF.

Collection and Reduction of Intensity Data

The space group was determined by preliminary oscillation and Weissenberg photographs (systematic absences hol, $l = 2n + 1$ and oko, $k = 2n + 1$). Complete crystal data and parameters for data collection are reported in Table I. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 15 automatically centered reflections in the range $23° < 2\theta < 25°$ on a SYNTEX $P2_1$ diffractometer with Zr-filtered MoKα radiation. The crystal was mounted with its b axis almost parallel to the φ axis of the instrument. The intensities of three standards monitored after every 67 reflections were stable with a scatter of less than 3% from their respective means. The data were reduced with the Syntex XTL programs [12]. The integrated intensity was calculated as $I = (Ns - (ts/tB)(B1 + B2))(SR)$ and the standard deviation as $\sigma(I) = (SR)(Ns + (ts/tB)^2\text{-}(B1 + B2))^{1/2}$ where Ns is the total scan count, B1 and B2 the two background counts, ts and tB the scan and total background times respectively and SR is the scan rate. Lorentz and polarization but no absorption corrections (= 14.4 cm^{-1}) were applied. Scattering factors were taken from the International Tables [13].

TABLE I. Summary of Crystal and Intensity Collection Data.

compd	Ce(salophen)$_2$
formula	$C_{40}H_{28}N_4O_4Ce$
fω	768.81
a, Å	11.090(2)
b, Å	16.332(3)
c, Å	18.916(3)
β, deg	70.10(2)
V, Å^3	3221.5
Z	4
D_{calcd}, g/cm^3	1.585
D_{measd}, g/cm^3	1.57
space group	$P2_1/C$
cryst. dimens, mm	0.20 × 0.30 × 0.35
cryst. shape	paralleliped with {100}, {010}, {001}
radiation	Mok$\bar{a}$ (λ = 0.71069 Å)
μ, cm^{-1}	14.4
scan type	$\omega - 2\theta$
scan speed	variable with 1° 2∂/min for weak refls.
scan range	0.8° below Ka$_1$ to 0.8° above Ka$_2$
bkgd counting	one half of scan time
2∂ limit, deg	46.5
data collected/unique	5127/4649
data used	4043 with $I \geqslant 2.5\sigma(I)$
data form	hkl and hk$\bar{l}$
error in obsn of unit wt	1.5
R	0.038
Rw	0.050

Solution and Refinement of the Structure

The position of the Ce atom was deduced from a Patterson synthesis. Two subsequent structure factor-Fourier calculations revealed the positions of all the non-hydrogen atoms. Refinement was carried out by blocked full matrix least-squares calculation in which $\Sigma\omega\Delta^2$ was minimized using the SHELX76 program [12]. One block contained the Ce atom, the coordination sphere and C7, C14, C27 and C34. Each of the other three blocks contained two phenyl rings. The weight for each reflection was initially unity and in the final cycles given by $\omega = (\sigma(F_o)^2 + cF_o{}^2)^{-1}$ where $c = 0.001$ was chosen such that the average values for $\omega\Delta^2$ for ranges of increasing F_o were almost constant. Isotropic refinement converged to an $R(=||F_o| - |F_c||/\Sigma|F_o|)$ of 0.078 and anisotropic refinement to $R = 0.048$. At this point the positions of the hydrogen atoms were located from a difference-Fourier map. These were included in the refinement as isotropic hydrogens riding on anisotropic carbon atoms at a fixed distance of 0.98 Å with their U's free to refine independently. The last two cycles of refinement included an empirical isotropic extinction parameter and they converged to a final value of $R = 0.0374$ and $R\omega = |\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2|^{1/2} = 0.0504$ for 4041 reflections having $I \geqslant 2.5\sigma(I)$. The reflections 100 and 012, badly affected by secondary extinction, were given zero weight. Anomalous dispersion corrections were applied to all non-hydrogen atoms. The final difference-Fourier map contained no peaks higher than 0.5 e/Å^3.

Results and Discussion

The final positional and thermal parameters appear in Tables II and III, while the observed and calculated structure amplitudes are available from the author. A perspective drawing of Ce(salophen)$_2$ appears in Fig. 1 and bond distance and angles along with their standard deviations are given in Fig. 2. The six phenyl groups are normal with an average C–C bond length of 1.389 (7, 17, 34) Å and an average C–C–C bond angle of 120.0 (5, 12, 17)° [14]. All other bond distances within the ligands are in excellent agreement with those of the corresponding Zr and Th complexes [15, 16]. The nitrogen atoms are trigonal planar with the sum of the three angles about each one being 360.0° (within one standard deviation).

TABLE II. Positional (×10^4) and Thermal (×10^3) Parameters with e.s.d.s in Parentheses. The general temperature factor expression is $\exp(-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{12}hka^*b^* + \ldots)$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	537.1(2)	2606.1(1)	3949.9(1)	34.9(2)	41.6(2)	30.2(2)	1.9(1)	−9.4(1)	0.3(1)
O1	2282(3)	2497(2)	4236(2)	49(2)	62(2)	44(2)	8(1)	−21(1)	−6(1)
C1	3488(4)	2278(3)	3847(3)	41(2)	53(2)	58(2)	9(2)	−25(2)	−16(2)
C2	4091(5)	1695(3)	4154(3)	54(2)	61(2)	78(2)	8(2)	−87(2)	−12(2)
C3	5353(5)	1474(3)	3761(3)	63(2)	67(2)	97(2)	24(2)	−46(2)	−24(2)
C4	6041(5)	1839(4)	3084(3)	48(2)	82(2)	98(2)	16(2)	−26(2)	−34(2)
C5	5466(5)	2422(3)	2784(4)	41(2)	72(2)	78(2)	6(2)	−15(2)	−23(2)
C6	4168(5)	2642(3)	3154(3)	39(2)	57(2)	55(2)	1(2)	−14(2)	−19(2)
C7	3618(4)	3239(3)	2797(3)	42(2)	56(2)	50(2)	−7(2)	−7(2)	−7(2)
N1	2410(3)	3387(2)	2961(2)	36(2)	46(2)	43(2)	−2(1)	−7(1)	−5(1)
C8	2031(4)	4002(3)	2545(2)	47(2)	42(2)	43(2)	−15(2)	−13(2)	5(2)
C9	2658(5)	4154(3)	1751(3)	56(2)	63(2)	51(2)	−12(2)	−9(2)	1(2)
C10	2195(5)	4757(3)	1422(3)	76(2)	73(2)	50(2)	−20(2)	−14(2)	20(2)
C11	1134(5)	5201(3)	1801(3)	78(2)	61(2)	64(2)	−9(2)	−27(2)	14(2)
C12	476(5)	5035(3)	2548(3)	65(2)	46(2)	56(2)	−0(2)	−23(2)	4(2)
C13	921(4)	4431(3)	2929(2)	48(2)	43(2)	40(2)	−7(2)	−14(2)	5(2)
N2	254(3)	4172(2)	3685(2)	42(2)	40(2)	45(2)	3(1)	−14(1)	−2(1)
C14	−466(4)	4702(3)	4143(2)	48(2)	44(2)	56(2)	1(2)	−24(2)	−3(2)
C15	−1274(4)	4550(3)	4911(2)	42(2)	55(2)	50(2)	2(2)	−19(2)	−14(2)
C16	−2170(4)	5153(3)	5269(3)	50(2)	61(2)	68(2)	13(2)	−25(2)	−21(2)
C17	−3009(5)	5042(3)	5991(3)	50(2)	80(2)	68(2)	17(2)	−21(2)	−34(2)
C18	−2934(5)	4334(4)	6365(3)	56(2)	88(2)	54(2)	−1(2)	−6(2)	−18(2)
C19	−2038(4)	3745(3)	6043(3)	61(2)	68(2)	44(2)	7(2)	−4(2)	−15(2)
C20	−1185(4)	3835(3)	5316(2)	43(2)	56(2)	40(2)	2(2)	−14(2)	−14(2)
O2	−300(3)	3278(2)	5022(2)	50(2)	61(2)	40(2)	10(1)	−13(1)	−5(1)
O3	1467(3)	1706(2)	3036(1)	52(1)	43(1)	35(1)	2(1)	−12(1)	2(1)
C21	2000(4)	1751(2)	2297(2)	50(2)	38(2)	31(2)	−7(2)	−6(1)	−6(1)
C22	3225(4)	1437(3)	1947(2)	60(2)	50(2)	40(2)	8(2)	−10(2)	−8(2)
C23	3799(5)	1481(3)	1180(3)	67(2)	68(2)	47(2)	8(2)	−3(2)	−7(2)
C24	3176(5)	1825(3)	727(3)	72(2)	72(2)	36(2)	0(2)	−8(2)	−4(2)
C25	1970(5)	2139(3)	1060(2)	70(2)	61(2)	35(2)	−5(2)	−16(2)	−2(2)
C26	1367(4)	2136(3)	1845(2)	51(2)	45(2)	38(2)	−9(2)	−14(2)	0(2)
C27	154(5)	2537(2)	2161(3)	53(2)	50(2)	41(2)	−6(2)	−22(2)	4(2)
N3	−371(3)	2756(2)	2852(2)	44(2)	45(2)	38(2)	−1(1)	−17(1)	1(1)
C28	−1529(4)	3220(3)	3077(2)	37(2)	54(2)	48(2)	0(2)	−20(2)	2(2)
C29	−1861(4)	3792(3)	2640(3)	54(2)	63(2)	70(2)	0(2)	−30(2)	9(2)
C30	−2949(5)	4279(3)	2957(3)	74(2)	71(2)	85(2)	11(2)	−38(2)	8(2)
C31	−3678(5)	4199(4)	3702(3)	60(2)	73(2)	103(2)	18(2)	−34(2)	−11(2)
C32	−3374(4)	3622(3)	4149(3)	41(2)	68(2)	70(2)	6(2)	−18(2)	−9(2)
C33	−2307(4)	3128(3)	3832(3)	35(2)	54(2)	63(2)	−1(2)	−23(2)	−2(2)
N4	−1896(4)	2527(2)	4252(2)	38(2)	56(2)	37(2)	−3(1)	−11(1)	2(1)
C34	−2753(4)	2114(3)	4748(2)	40(2)	66(2)	45(2)	−2(2)	−7(2)	−6(2)
C35	−2513(4)	1470(3)	5205(2)	55(2)	61(2)	37(2)	−8(2)	−6(2)	−1(2)
C36	−8582(5)	1076(3)	5714(3)	63(2)	75(2)	60(2)	−18(2)	−1(2)	8(2)
C37	−8452(6)	423(4)	6138(3)	92(2)	76(2)	67(2)	−29(2)	1(2)	10(2)
C38	−2248(6)	164(3)	6076(3)	103(2)	56(2)	48(2)	−1(2)	5(2)	6(2)
C39	−1178(5)	549(3)	5604(2)	84(2)	48(2)	40(2)	7(2)	1(2)	4(2)
C40	−1286(4)	1199(3)	5141(2)	60(2)	43(2)	29(2)	−5(2)	0(2)	0(2)
O4	−249(3)	1503(2)	4643(2)	55(2)	56(2)	45(2)	6(1)	−9(1)	7(1)

The coordination polyhedron is SAP with each ligand spanning sss edges [2]. Although the donor atoms of each ligand are not far from planar (maximum deviation is 0.06 Å for N1 of one ligand and 0.02 Å for N3 of the other) the ligands as a whole are quite distorted from planarity as is evident from Fig. 1. The puckering occurs most significantly at the nitrogen atoms with the torsion angles 3 and 5 around the N1–C8, N2–C13, N3–C28 and N4–C33 bonds being the largest (Table IV). Since the coordination polyhedron is SAP the N and O donor atoms do not sort into A and B sites according to Orgel's rule [8, 9]. This is of course not surprising since factors other than the electronic one are also

TABLE III. Positional ($\times 10^3$) and Isotropic Thermal Parameters ($\times 10^3$) of Hydrogen Atoms. E.s.d.'s in Parentheses.

Atom	x	y	z	U_{iso}
H2	362	144	464	47(3)
H3	576	105	396	56(3)
H4	693	168	282	55(3)
H5	595	268	230	55(3)
H7	421	356	239	52(3)
H9	342	383	149	54(3)
H10	264	486	88	54(3)
H11	83	563	154	54(3)
H12	−30	534	281	53(3)
H14	−46	526	395	52(3)
H16	−220	566	500	52(3)
H17	−364	546	623	54(3)
H18	−353	424	687	55(3)
H19	−199	325	633	52(3)
H22	368	118	225	51(3)
H23	466	126	94	54(3)
H24	359	184	17	52(3)
H25	151	237	74	50(3)
H27	−31	265	182	51(3)
H29	−133	385	210	55(3)
H30	−319	468	264	53(3)
H31	−442	455	391	53(3)

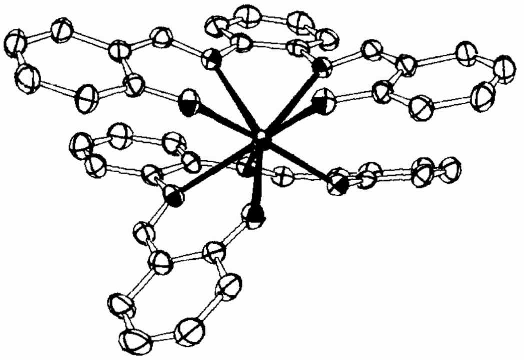
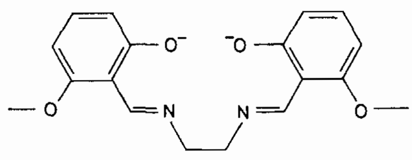
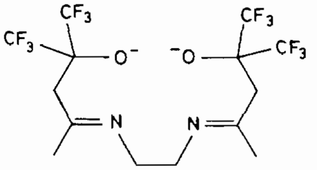


Fig. 1. ORTEP plot of Ce(salophen)$_2$. Thermal ellipsoids are at the 50% probability level. H atoms are not shown.

expected to be at work here. In Table V we compare relevant parameters of five similar complexes. The metals involved are Th^{4+}, Zr^{4+} and Ce^{4+} and the ligands are salophen, N,N′-di-3-methoxysalicylidene-1,2-ethylenediamine(2−), (3MeOSalen), and 1,1,1,12,12,12-hexafluoro-2,11-bis(trifluoromethyl)-4,9-dimethyl-2,11-diolato-5,8-diazadodeca-4,8-diene-(2−), (fluorodiene). We have used the reported atomic coordinates [17] to calculate the dihedral angles [4, 5] δ, φ and ω (Table V) and the relevant tortion angles (Table IV). Three of the complexes are DOD and two are SAP. Here we must stress a point that was made by Porai-Koshits and Aslanov [4] as to the weakness of the ω angle criterion [3] in differentiating between a DOD and a SAP polyhedron.



3 MeOSalen



Fluorodiene

The angle ω between the body-diagonal trapezoids is 90° for an ideal DOD and 79.3° for an ideal SAP. But as pointed out there are several distortions which can change ω while the polyhedron retains its characteristic shape. We see from Table IV that according to the ω criterion all five complexes are DOD. However, the dihedral angle criterion [4–6] (δ and φ), which is more powerful, clearly distinguishes the three DOD from the two SAP complexes. Table V also points out the necessity of calculating these dihedral angles because sometimes it is difficult to assign the correct geometry by simple inspection of a drawing. It is reported [18] that the structure of Ce(fluorodiene)$_2$ 'approximates a square antiprism although it is obvious that the bases of the prism are not truly planar'. In fact the dihedral angles across the diagonals of these 'bases' are 24.8° and 28.1° δ_1 and δ_2 at Table V. They should be 0° for SAP and 29.5° for DOD. Along with δ_3, δ_4 and the φ angles they suggest that the structure is best described as a DOD.

It appear that on the basis of Orgel's rule alone we cannot rationalize the results of Table V. Instead we shall examine it in terms of four additional parameters in the hope of finding out the factors that determine the geometry of the coordination polyhedron. These parameters are: the ligand orientation, the ligand flexibility, the size of the metal and the maximum distance of an atom from the mean plane of the coordinating atoms of the ligand to which it belongs. First we point out the similarity of the structures of Ce(salophen)$_2$ and Th(salophen)$_2$. For the same ligand and metals of similar size (Th, Ce), Table IV and Table V show that the various geometrical parameters of the two structures, δ, φ, ω and torsion angles are remarkably similar. Also there are no surprises in the metal-ligand distances and angles. The long Ce–N distances relative to the Ce–O distances are quite typical of this type of structure (Table IV).

Now, we see from Table V that when the two quadridentate ligands are oriented 'perpendicular' to each other (meridional orientation) the coordination polyhedron is DOD and when they are 'parallel' to each other (sandwich orientation) the polyhedron

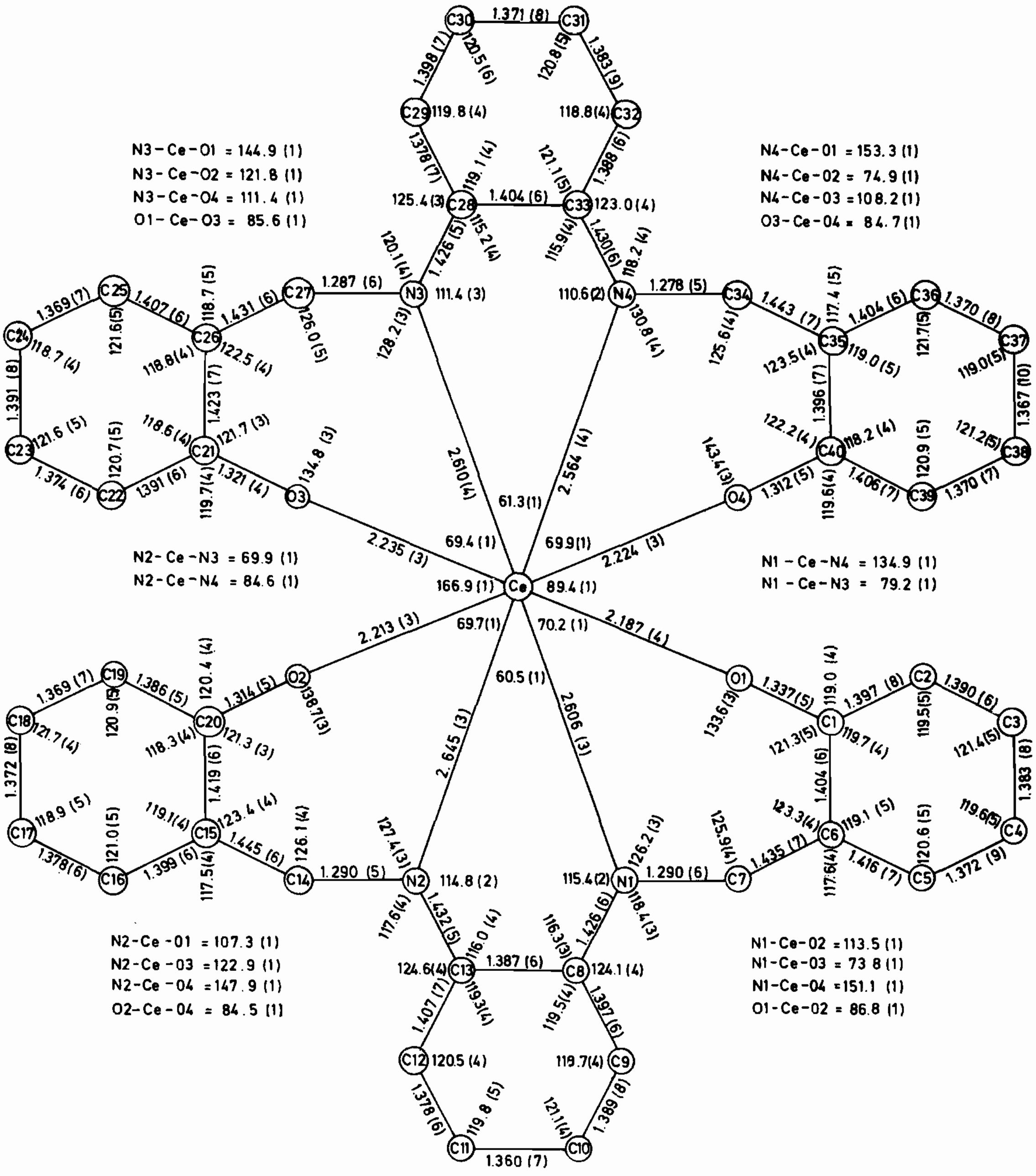


Fig. 2. Interatomic bond distances and angles for Ce(salophen)$_2$ (standard deviations in parentheses).

is SAP. So we may ask what determines the orientation of the ligands. If we look at the three complexes with the salophen ligand we see that in the case of Zr (small radius) the orientation is 'perpendicular'. So it appears that if the metal is small enough, salophen can wrap around it in meridional orientation but if the metal is large (Th, Ce) the ligands are forced above and below the metal in a sandwich orientation.

However, if the ligand has enough flexibility, as is the case for 3MeOSalen and fluorodiene, then it can wrap around even the large metal ions. Now, it is clear that the three ligands in question can be arranged in terms of their flexibility [20] in the order of salophen < 3MeOSalen < fluorodiene. We see in Table IV that the torsion angles 3 and 5 range between |144.3°| and |156.1°| for salophen while for the other two ligands the range is |130.3°| to |142.3°|. The latter two ligands have the extra flexibility at torsion angle 4 which varies between |49.4°| and |64.8°|, while for salophen it is close to zero. Fluorodiene has additional flexibility at angles 1 and 7. For the fluorodiene ligand there is an additional factor, probably the determining one, which forces this ligand into a meridional orientation. In the Ce(fluoro-

TABLE IV. Torsion Angles (deg) and Average Metal–Ligand Distances (Å).

Torsion angle / Compound	1 C1–C6–C7–N1 C21–C26–C27–N3	2 C6–C7–N1–C8 C26–C27–N3–C28	3 C7–N1–C8–C13 C27–N3–C28–C33	4 N1–C8–C13–N2 N3–C28–C33–N4	5 C8–C13–N2–C14 C28–C33–N4–C34	6 C13–N2–C14–C15 C33–N4–C34–C35	7 N2–C14–C15–C20 N4–C34–C35–C40	M–N M–O	(M–N)–(M–O)
Ce(salophen)$_2$ [a]	–16.1	–179.7	–148.6	–3.3	155.2	176.0	13.5	2.606	
	15.9	174.2	153.3	–5.8	–144.3	178.1	–2.1	2.214	0.392
Th(salophen$_2$ [b]	14.5	176.1	152.4	–3.4	–149.6	–172.6	–12.1	2.655	
								2.287	0.368
Zr(salophen)$_2$ [b]	–6.1	168.4	156.1	–2.4	–152.7	–170.9	8.8	2.428	
	11.7	–171.9	–150.8	0.9	150.6	174.0	–14.0	2.097	0.331
Th(3MeOSalen)$_2$ [b]	–1.1	–176.9	–137.3	–62.4	–135.9	–173.5	5.3	2.63	
	–5.2	–178.4	–137.8	–49.4	–142.3	179.8	12.8	2.28	0.35
Ce(fluorodiene)$_2$ [b]	–59.2	–174.7	133.3	62.1	130.3	–174.7	–54.2	2.623	
	61.0	171.4	–136.0	–64.8	–132.6	171.4	59.4	2.211	0.412

[a] This study. [b] Reference [17]. [c] The torsion angle A–B–C–D equals the angle between the planes defined by the atoms A, B, C, and B, C, D. The angle is considered (+) if the bond in front, A–B, has to be rotated clockwise to eclipse bond C–D.

diene)$_2$ complex there are fluorine atoms on each ligand which are more than 2.0 Å above and below the mean plane of the coordinating atoms of the particular ligand. If these ligands were to take the sandwich orientation these fluorine atoms would be 'touching' on atoms of the other ligand. To avoid this they assume the meridional orientation.

In summary, there is a small driving force towards a DOD geometry, the basis of which is Orgel's rule, as in the case of Zr(salophen)$_2$. If the metals are large (Ce^{4+}, Th^{4+}) and the ligand is 'inflexible' (salophen) this driving force is not sufficient to force the necessary torsional distortions on the ligand so it can wrap around the larger metal ions: the ligands assume the sandwich orientation and a SAP geometry. However, when the ligands are 'flexible' (3MeOSalen, fluorodiene) they can achieve the torsion angles necessary for a meridional orientation and a DOD geometry. According to this reasoning we expect that Ce(salen)$_2$ and Ce(3MeOSalen)$_2$ will have the meridional orientation and a DOD geometry. We are presently trying to crystallize these complexes to solve the structure of at least one of these.

Now, for the two ligands in a sandwich orientation to achieve the SAP geometry they must be rotated with respect to each other either 45° or 135° approximately. It happens also that at either of these angles the six phenyl rings, in the salophen complexes, would be in the staggered orientation. It is not immediately clear why both in the present study (Fig. 3) and in the Th(salophen)$_2$ [16] the preferred angle is 45°. There is also the question of why the ligands in a sandwich orientation do not achieve a DOD geometry. We see at least two reasons.

First a DOD geometry would necessitate large distortions of the ligand and second the small driving force towards a DOD geometry (Orgel's rule) does not exist since in the sandwich orientation the coordinating atoms cannot possibly sort into A and B sites.

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TABLE V. Dihedral Angle Parameters (deg).

Compound	Polyhedron	Ligand orient.	δ_1	δ_2	δ_3	δ_4	φ_1 or φ_{av}	φ_2	ω
Ce(salophen)$_2$ [a]	SAP	sandwich	7.0	2.6	56.5	55.9	28.6	30.0	88.2
Th(salophen)$_2$ [b]	SAP	sandwich	3.6	3.6	58.8	58.8	35.5	35.5	87.4
Zr(salophen)$_2$ [b]	DOD	meridional	28.0	19.6	22.5	25.8	0.8		89.2
Th(3MeOSalen)$_2$ [b]	DOD	meridional	15.9	21.1	31.4	35.8	10.0	9.7	89.0
Ce(fluorodiene)$_2$ [b]	DOD	meridional	24.8	28.1	24.1	22.4	13.8	10.4	89.8
Reference DOD	DOD		29.5	29.5	29.5	29.5	0	0	90
Reference SAP	SAP		0	0	52.4	52.4	24.5	24.5	79.3

[a] This study. [b] Reference

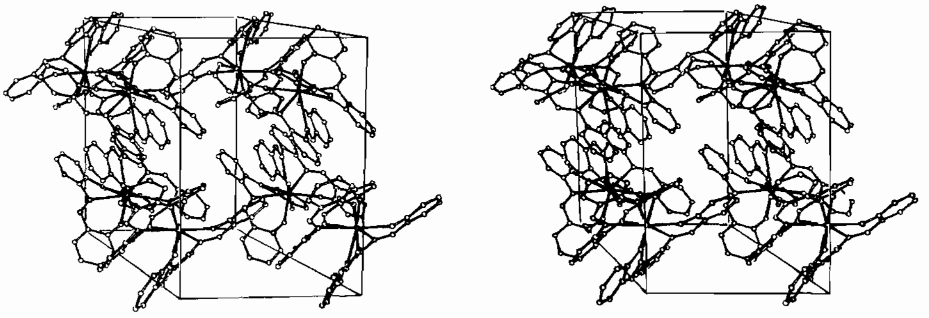

Fig. 3. Stereoscopic view of the molecular packing.

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17 In the case of Zr(salophen)$_2$ we used the reported angles [15]. In the case of Ce(fluorodiene)$_2$ there are errors in the reported atomic coordinates [18]; for O2 $y = -0.1220$ and not 0.1220 and for N2 $x = 0.2994$ and not 0.0408. There are other errors as well but not in the backbone of the molecule which is involved in our calculations. For Th(3MeOSalen)$_2$ we used the coordinates of reference [19].

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20 By flexibility we mean the ability of the ligand backbone atoms, O1, C1, C6, C7, N1, C8, C13, N2, C14, C15, C20, O2, to achieve a nonplanar arrangement. A perfectly planar arrangement requires the torsion angles of Table III to be either 0° or 180°. So a flexible ligand can achieve torsion angles from 0° to 180°.