O212—S21—O211	100.58 (9)	C201—C202—C203	118.2 (4)
O213—S21—O211	107.60 (11)	C202—C203—C204	113.1 (4)
O214—S21—O211	108.40 (11)	C302—C203—C304	117.7 (4)
O213—S21—O212	112.00 (11)	C203—C204—C205	115.5 (4)
O214—S21—O212	114.78 (12)	C204—C205—C206	114.7 (4)
O214—S21—O213	112.49 (12)	C304—C205—C306	119.3 (4)
O322—S22—O221	103.2 (2)	C205—C206—C207	115.5 (4)
O223—S22—O221	111.8 (2)	C206—C207—C208	115.8 (4)
O324—S22—O221	109.2 (2)	C306—C207—C308	119.6 (4)
O222—S22—O221	102.6 (2)	C207—C208—C209	115.4 (5)
O224—S22—O221	103.8 (2)	C208—C209—C210	116.2 (4)
O323—S22—O221	100.0 (2)	C308—C209—C310	117.8 (4)
O223—S22—O222	114.1 (2)	C209—C210—C211	115.0 (4)
O223—S22—O224	112.5 (2)	C210—C211—C212	114.4 (4)
O222—S22—O224	111.1 (2)	C310—C211—C312	114.2 (4)
O322—S22—O323	115.7 (3)	C211—C212—O221	108.5 (4)
O324—S22—O323	108.5 (3)	C201—C302—C203	120.8 (4)
C11—O111—S11	115.8 (2)	C203—C304—C205	119.4 (5)
C201—O211—S21	117.07 (15)	C205—C306—C207	119.4 (4)
C212—O221—S22	115.7 (2)	C207—C308—C209	118.2 (5)
C312—O221—S22	118.1 (3)	C209—C310—C211	115.5 (5)
O111—C11—C12	107.8 (2)	C211—C312—O221	108.1 (4)
C11—C12—C13	110.9 (2)		

O111—C11—C12—C13	173.1 (2)
O211—C201—C202—C203	53.7 (5)
O211—C201—C302—C203	−50.6 (6)
C310—C211—C312—O221	−175.2 (5)

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

Structure solution in space group $P1$ gave the same disorder as in $P\bar{1}$, i.e. all atom positions including disordered pairs found in $P\bar{1}$ were also found in $P1$. Therefore, the disorder cannot be explained by a wrong choice of the space group. The positions of H atoms bonded to C atoms were calculated at a distance of 0.97 Å, their U values set to 1.3 times the equivalent U values of their bonding partners, and were refined riding on the C atoms. The H atoms of the water molecules were found from difference Fourier synthesis and refined without constraints. Two independent population parameters were refined, one for the disordered chain, one for the disordered sulfate group. They were 0.479 (5)/0.521(5) for the chain and 0.412 (8)/0.588(8) for the sulfate group. Refinement of the population parameter of the water molecule gave 0.99 (1), therefore it was fixed to 1.0 in the final refinement cycles. After refinement, the highest difference density peak was found near the S atom of the disordered sulfate group.

Data collection: Enraf–Nonius (1977) CAD-4 diffractometer system. Cell refinement: Enraf–Nonius (1977) CAD-4 diffractometer system. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SCHAKAL92* (Keller, 1992). Software used to prepare material for publication: *SHELXL93*.

References

Abrahamsson, S., Dahlén, B., Löfgren, H. & Pascher, I. (1978). *Prog. Chem. Fats Lipids*, **16**, 125–143.

Coiro, V. M., Mazza, F. & Pochetti, G. (1986). *Acta Cryst.* C42, 991–995.

Coiro, V. M., Manigrasso, M., Mazza, F. & Pochetti, G. (1987). *Acta Cryst.* C43, 850–854.

Enraf–Nonius (1977). *CAD-4 Operations Manual.* Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Keller, E. (1992). *SCHAKAL92. A Computer Program for the Graphic Representation of Molecular and Crystallographic Models.* University of Freiburg, Germany.

Rudert, R., Vollhardt, D. & Czichocki, G. (1996). *Z. Kristallogr.* **211**, 43–45.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sundell, S. (1977). *Acta Chem. Scand. Ser. A*, **31**, 799–807.

Two Derivatives of Lithium Isodicyclopentadienide: [(1,2,3,3a,7a-η)-4,5,6,7-Tetrahydro-4,7-methanoindenido](N,N,N',N'-tetramethylethylenediamine)lithium and Bis(1,4,7,10-tetraoxacyclododecane)lithium(1+) Bis[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-4,7-methanoindenido]lithate(1-)

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Abstract

Selective crystallization of a solution of lithium isodicyclopentadienide, (isodiCp)Li, in dry thf or diethyl ether under argon has produced two lithium complexes: (isodiCp)Li(TMEDA), [Li($C_{10}H_{11}$)($C_6H_{16}N_2$)], (4), and [Li(12-crown-4)$_2$]$^+$.[Li(isodiCp)$_2$]$^-$, [Li($C_8H_{16}O_4$)$_2$]-[Li($C_{10}H_{11}$)$_2$], (5). In (4) the Li$^+$ ion is coordinated to the two N atoms of the disordered TMEDA and is η^5-coordinated to the Cp ring of the isodiCp ligand. The Li–(Cp ring centroid) distance is 1.906 (7) Å. In (5) there are two independent half-molecules of the anion and one molecule of the cation in the asymmetric unit. In each anion, the Li$^+$ ion occupies a crystallographic inversion center and is η^5-coordinated to the two Cp rings of two isodiCp ligands. The Cp rings are in a staggered arrangement, as required by the inversion center. The Li—(Cp

ring centroid) distances for the two anions are 1.987 (3) and 2.008 (3) Å. In the cation of (5), the Li⁺ ion is co-ordinated to two 12-crown-4 ligands, one of which is disordered. Both (4) and (5) exhibit *exo* coordination of the Li⁺ ion to the isodiCp ligand, with a resultant slight *endo* bending of this ligand.

Comment

During the past decade, lithium isodicyclopentadienide, (1) [(isodiCp)Li], has emerged as the parent of a series of bicyclic fused anions that exhibit an amazing capability for the stereoselective capture of electrophiles (Paquette, Charumilind, Kravetz, Böhm & Gleiter, 1983; Paquette, Charumilind & Gallucci, 1983; Gallucci, Gautheron, Gugelchuk, Meunier & Paquette, 1987; Paquette, Moriarty, Meunier, Gautheron & Crocq, 1988; Paquette, Moriarty, Meunier *et al.*, 1989; Sornay, Meunier, Gautheron, O'Doherty & Paquette, 1991; Paquette, Moriarty & Rogers, 1989; Moriarty, Rogers & Paquette, 1989; Paquette, Moriarty, McKinney & Rogers, 1989; Sivik, Rogers & Paquette, 1990; Paquette & Sivik, 1992; Rogers, Sivik & Paquette, 1993). Whereas co-valent bonding to (1) occurs predominantly from the *endo* direction at 195 K, a switch-over to the *exo* face is seen in the vicinity of 293 K. This remarkable dependence on temperature is now recognized to be a function of the detailed structural features of (1) and its congeners in thf solution (Paquette *et al.*, 1990; Bauer, O'Doherty, Schleyer & Paquette, 1991; Bauer, Sivik, Friedrich, Schleyer & Paquette, 1992; Paquette, Sivik, Bauer & Schleyer, 1994). By means of one- and two-dimensional NMR analysis involving the use of 96% ⁶Li-enriched lithium in thf-d_8 as solvent, it has proven possible to demonstrate that the contact ion pair (2), with the metal ion η^5-coordinated *exo*, is the dominant species near room temperature. As these solutions are cooled, the concentration of the sandwich dimer (3) progressively increases until it predominates at 195 K. These structurally distinctive aggregates are believed to be stereoselective in their reactions toward complementary reagents.

(1)

(2)   (3)
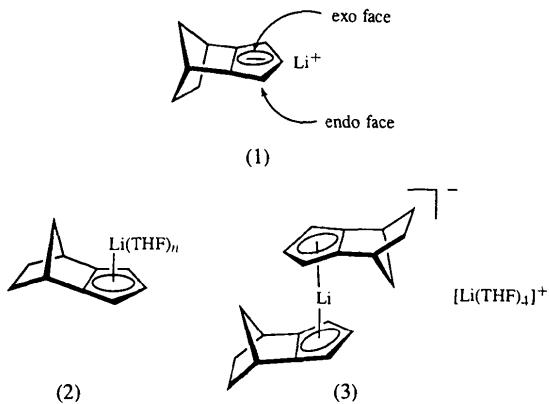
Recently, success has been realised in obtaining derivatives of (2) and (3) as crystalline compounds (Zaegel *et al.*, 1994). As a result, the earlier conclusions concerning their reaction stereochemistry have been accorded additional support. A derivative of the contact ion pair (2) has been isolated as the tetramethyl-ethylenediamine (TMEDA) complex (4). The sandwich dimer (3) has been co-crystallized with [Li(12-crown-4)₂]⁺ to give (5). Presented herein are detailed descriptions of the crystal structures of (4) and (5). This study has demonstrated that crystalline derivatives of (isodi-Cp)Li can be obtained from an equilibrating system in a selective manner.

(4)

(5)
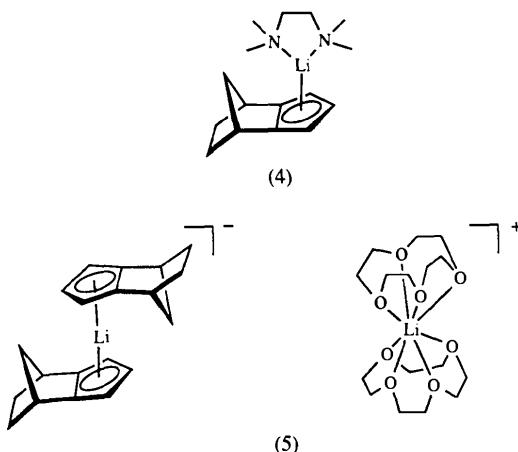
In (4) the Li atom is coordinated to the two N atoms of the TMEDA group and to the Cp ring of the isodiCp ligand. The Li—C distances for the Cp ring range from 2.219 to 2.264 (7) Å so that the Li–Cp interaction may be described as η^5. The distance between the Li atom and the ring centroid of the Cp ring is 1.906 (7) Å, which is comparable with distances observed in Li(C₅H₄CH₃)TMEDA (Hammel, Schwarz & Weidlein, 1990) of 1.92 Å and in Li[C₅H₄Si(CH₃)₃]TMEDA (Lappert, Singh, Engelhardt & White, 1984) of 1.93 Å. The orientation of the iso-diCp ligand with respect to the Li atom is *exo*. Atoms C6 and C9 are 0.210 (6) and 0.204 (6) Å, respectively, from the least-squares plane through C1—C2—C3—C4—C5 and on the opposite side of this plane from the Li atom. This results in a slight *endo* bending in the ligand about the C1—C5 bond. The bending can also be described by the dihedral angle between the least-squares planes through C1—C2—C3—C4—C5 and C6—C5—C1—C9, which is 8.4 (1)° for this structure. The N1—Li—N2 angle of 83.5 (2)° is as expected for TMEDA bound to Li.

Structure (5) can be considered as an ion pair consisting of [Li(isodiCp)₂]⁻ and [Li(12-crown-4)₂]⁺. There is little difference between the two independent molecules of [Li(isodiCp)₂]⁻ (labeled as A and B) in the asymmetric unit. Each shows an *exo* arrangement of
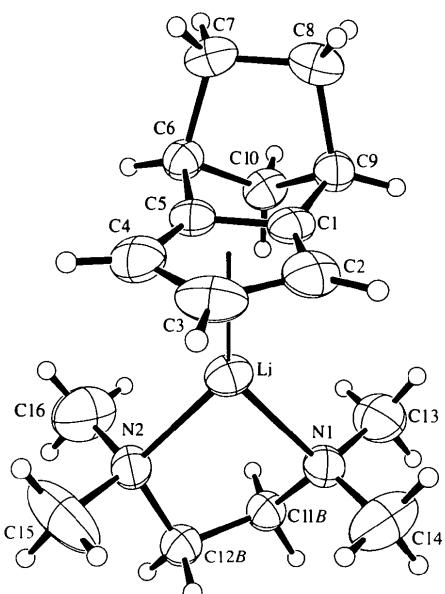
Fig. 1. Molecular structure of (4) drawn with 30% probability displacement ellipsoids for the non-H atoms. Only one of the ethylene orientations of the disordered TMEDA ligand is shown. The H atoms are represented by circles of an arbitrary radii.

the isodiCp ligands with respect to Li, with an η^5 interaction between each Cp ring and the Li atom. In *B* the Li—C distances for the Cp ring are in a narrower range [2.300 (3)–2.341 (3) Å] than for *A* [2.292 (3)–2.389 (3) Å]. The Li–(ring centroid) distances are 1.987 (3) for *B* and 2.008 (3) Å for *A*. These distances are all significantly longer than the analogous distances in (4). Other structures with Li—C distances comparable with those in (5) are [C$_5$H$_2$(SiMe$_3$)$_3$]Li(pmdeta) [2.304–2.350 (6) Å; Jutzi, Schlüter, Krüger & Pohl, 1983], Li[C$_5$H$_2$(SiMe$_3$)$_3$]TMEDA [2.277–2.378 (16) and 2.287–2.364 (15) Å; Jutzi, Schlüter, Pohl & Saak, 1985], (indenyl)Li(TMEDA) [2.279–2.379 (4) Å; Rhine & Stucky, 1975] and (12-crown-4)Li(η^5-C$_5$H$_5$) [2.344–2.419 (5) Å; Chen, Jutzi, Leffers, Olmstead & Power, 1991]. Although the Li—C distances in (5) are greater than those in (4), the metrical parameters of the isodiCp ligands in (4) and (5) are in agreement within two or three e.s.d.'s. The isodiCp ligands exhibit the same degree of bending in (5) as in (4): atoms C14*B* and C17*B* are each 0.202 (4) Å out of the best least-squares plane through C9*B*—C10*B*—C11*B*—C12*B*—C13*B*, and atoms C14*A* and C17*A* are 0.165 (3) and 0.179 (4) Å away from the analogous plane in molecule *A*. The *endo* bending of the ligand about the C9—C13 bond is away from the Li atom in both cases, as it is in (4). The dihedral angle which describes this bending [defined as above for structure (4)] is 6.9 (2) for *A* and 8.1 (2)° for *B*. Each Li atom is on an inversion center, so that the Cp rings are in a staggered arrangement and the isodiCp ligands point in opposite directions.
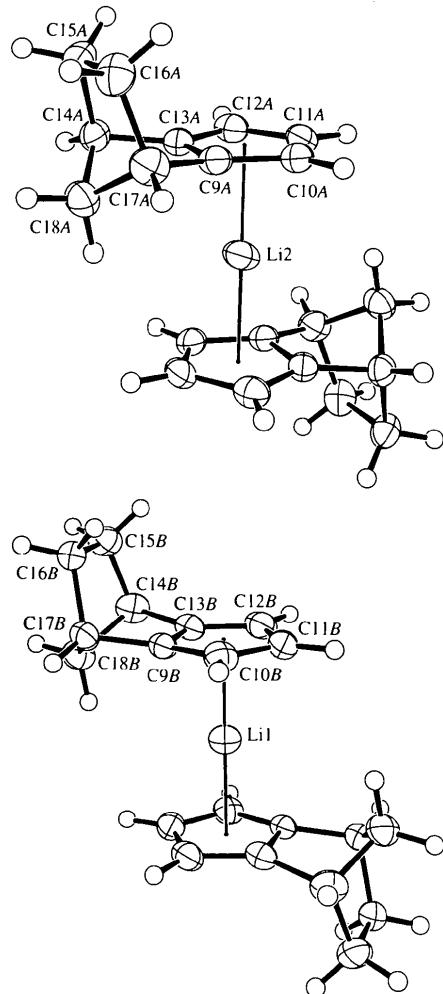
Fig. 2. Molecular structure of the two independent [(isodiCp)$_2$Li]$^-$ molecules of (5) drawn with 50% probability displacement ellipsoids. The H atoms are represented by circles of an arbitrary radii.
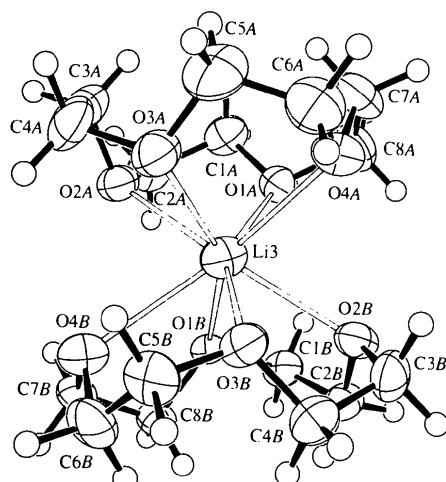

Fig. 3. Molecular structure of the cation of (5), [Li(12-crown-4)$_2$]$^+$, drawn with 50% probability displacement ellipsoids. The alternate orientation for crown *B* has been omitted for clarity. The H atoms are represented by circles of an arbitrary radii.

The $[Li(12\text{-crown-4})_2]^+$ cation of (5) has often been reported (Chen *et al.*, 1991; Power, 1988). The structure here is typical of earlier cases, with the Li atom coordinated to eight O atoms with a wide range of Li— O distances: 2.225 (7)–2.601 (7) Å. The arrangement of the O atoms about the Li$^+$ ion can be described as a distorted square antiprism with approximate D_{4d} symmetry.

Experimental

The synthesis of (4) involved adding TMEDA (3.84 mmol) dropwise to a suspension of (isodiCp)Li (2.10 mmol) in dry diethyl ether under Ar, concentrating the solvent to low volume after 3 h at room temperature, and cooling to 253 K. Air- and moisture-sensitive crystals were obtained in 80% yield. The data-collection crystal was mounted in a glass capillary under a nitrogen atmosphere.

The synthesis of (5) was carried out by dropwise addition of 12-crown-4 (1.76 mmol) to a solution of (isodiCp)Li (0.90 mmol) in dry thf, concentration of the solvent to low volume after 1 h at room temperature, and cooling to 253 K. Yellow air-sensitive crystals were obtained in 75% yield. The data crystal was coated with Paratone N and quickly placed in the liquid-nitrogen-cooled gas stream on the diffractometer (Hope, 1987). All X-ray work was performed at 203 K.

Compound (4)

Crystal data
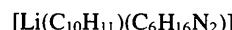
$[Li(C_{10}H_{11})(C_6H_{16}N_2)]$
$M_r = 254.34$
Monoclinic
$P2_1/c$
$a = 8.216 (2)$ Å
$b = 16.164 (2)$ Å
$c = 12.762 (2)$ Å
$\beta = 107.12 (2)°$
$V = 1619.7 (5)$ Å^3
$Z = 4$
$D_x = 1.043$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–13°$
$\mu = 0.060$ mm^{-1}
$T = 296$ K
Equidimensional chunk
$0.38 \times 0.38 \times 0.38$ mm
Pale tan

Data collection

Rigaku AFC-5S diffractom-
   eter
ω–2θ scans
Absorption correction:
   none
3197 measured reflections
2861 independent reflections
916 observed reflections
   $[I > 2\sigma(I)]$

$R_{int} = 0.038$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -15 \rightarrow 14$
6 standard reflections
   monitored every 150
   reflections
   intensity decay: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.189$
$S = 1.00$

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: none

2859 reflections
175 parameters
H-atom parameters not
   refined
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors
   from *International Tables
   for Crystallography* (1992,
   Vol. C, Tables 4.2.6.8 and
   6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (4)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
N1	−0.2844 (4)	0.8035 (2)	0.0639 (3)	0.0726 (10)
N2	0.0455 (4)	0.7972 (2)	0.2209 (3)	0.0675 (10)
C1	−0.2927 (6)	0.9991 (2)	0.2079 (4)	0.0592 (11)
C2	−0.2350 (7)	1.0238 (2)	0.1196 (4)	0.0776 (14)
C3	−0.0573 (8)	1.0264 (3)	0.1590 (5)	0.085 (2)
C4	−0.0030 (6)	1.0066 (2)	0.2708 (4)	0.0782 (13)
C5	−0.1506 (6)	0.9884 (2)	0.2998 (3)	0.0573 (10)
C6	−0.2172 (5)	0.9758 (2)	0.3964 (3)	0.0647 (11)
C7	−0.2950 (6)	1.0596 (3)	0.4186 (4)	0.0798 (14)
C8	−0.4492 (6)	1.0713 (3)	0.3165 (4)	0.0859 (14)
C9	−0.4468 (5)	0.9924 (2)	0.2470 (3)	0.0667 (12)
C10	−0.3833 (5)	0.9297 (2)	0.3399 (3)	0.0719 (13)
C11A†	−0.1662 (16)	0.7336 (7)	0.0664 (11)	0.062 (4)
C12A†	−0.0651 (19)	0.7199 (7)	0.1827 (11)	0.076 (5)
C11B‡	−0.2043 (9)	0.7220 (4)	0.1102 (9)	0.067 (3)
C12B‡	−0.0100 (10)	0.7310 (5)	0.1393 (8)	0.069 (3)
C13	−0.4555 (6)	0.7918 (3)	0.0748 (4)	0.112 (2)
C14	−0.2993 (8)	0.8283 (3)	−0.0476 (4)	0.133 (2)
C15	0.2083 (7)	0.8164 (4)	0.2056 (6)	0.169 (3)
C16	0.0681 (8)	0.7787 (4)	0.3351 (4)	0.140 (2)
Li	−0.1319 (9)	0.8958 (4)	0.1731 (5)	0.065 (2)

† Occupancy = 0.40 (2); U_{iso}.   ‡ Occupancy = 0.60 (2); U_{iso}.

Table 2. *Selected geometric parameters (Å, °) for (4)*

N1—C14	1.448 (5)	C2—Li	2.264 (7)
N1—C13	1.465 (5)	C3—C4	1.400 (6)
N1—C11A	1.484 (11)	C3—Li	2.219 (7)
N1—C11B	1.513 (8)	C4—C5	1.399 (5)
N1—Li	2.170 (7)	C4—Li	2.260 (7)
N2—C15	1.441 (5)	C5—C6	1.502 (5)
N2—C16	1.444 (5)	C5—Li	2.242 (7)
N2—C12B	1.468 (7)	C6—C10	1.535 (5)
N2—C12A	1.536 (13)	C6—C7	1.560 (5)
N2—Li	2.125 (7)	C7—C8	1.538 (5)
C1—C5	1.401 (5)	C8—C9	1.557 (5)
C1—C2	1.403 (5)	C9—C10	1.530 (5)
C1—C9	1.496 (5)	C11A—C12A	1.49 (2)
C1—Li	2.252 (7)	C11B—C12B	1.536 (12)
C2—C3	1.398 (5)		
C14—N1—C13	108.8 (4)	C3—C2—C1	106.4 (4)
C14—N1—C11A	95.6 (7)	C2—C3—C4	110.2 (4)
C13—N1—C11A	122.7 (7)	C5—C4—C3	106.1 (4)
C14—N1—C11B	121.7 (5)	C4—C5—C1	109.0 (4)
C13—N1—C11B	99.8 (5)	C4—C5—C6	143.0 (5)
C14—N1—Li	107.8 (3)	C1—C5—C6	106.8 (4)
C13—N1—Li	114.6 (3)	C5—C6—C10	99.7 (3)
C11A—N1—Li	105.0 (5)	C5—C6—C7	107.4 (3)
C11B—N1—Li	104.2 (4)	C10—C6—C7	98.7 (3)
C15—N2—C16	109.4 (4)	C8—C7—C6	103.4 (3)
C15—N2—C12B	99.6 (5)	C7—C8—C9	103.7 (3)
C16—N2—C12B	119.1 (5)	C1—C9—C10	100.2 (3)
C15—N2—C12A	128.1 (7)	C1—C9—C8	106.6 (3)
C16—N2—C12A	92.4 (6)	C10—C9—C8	99.2 (3)
C15—N2—Li	112.6 (4)	C9—C10—C6	95.5 (3)
C16—N2—Li	108.6 (3)	N1—C11A—C12A	107.7 (11)
C12B—N2—Li	107.4 (4)	C11A—C12A—N2	107.5 (11)
C12A—N2—Li	103.1 (5)	N1—C11B—C12B	108.2 (7)
C5—C1—C2	108.2 (4)	N2—C12B—C11B	109.0 (7)
C5—C1—C9	106.8 (4)	N2—Li—N1	83.5 (2)
C2—C1—C9	143.9 (5)		

Compound (5)

Crystal data

[Li(C$_8$H$_{16}$O$_4$)$_2$][Li(C$_{10}$H$_{11}$)$_2$]
M_r = 628.71
Triclinic
$P\overline{1}$
a = 11.818 (1) Å
b = 16.129 (2) Å
c = 9.871 (1) Å
α = 107.05 (1)°
β = 108.23 (1)°
γ = 88.70 (1)°
V = 1703.6 (4) Å^3
Z = 2
D_x = 1.225 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.5–15.0°
μ = 0.078 mm^{-1}
T = 203 K
Rectangular rod
0.50 × 0.31 × 0.31 mm
Pale yellow

Data collection

Rigaku AFC-5S diffractometer
ω–2θ scans
Absorption correction: none
6348 measured reflections
6003 independent reflections
3807 observed reflections
[$I > \sigma(I)$]

R_{int} = 0.025
θ_{max} = 25.0°
h = 0 → 14
k = −18 → 19
l = −11 → 10
5 standard reflections monitored every 150 reflections intensity decay: <1%

Refinement

Refinement on F
R = 0.054
wR = 0.056
S = 1.706
3807 reflections
468 parameters
H-atom parameters not refined
w = 1/$\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Extinction correction: Zachariasen (1963)
Extinction coefficient: 1.6 (1) × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1) (C, O, Li) and Stewart, Davidson & Simpson (1965) (H)

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (5)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
O1A	0.5565 (2)	0.1981 (1)	0.4620 (2)	0.0458 (7)
O2A	0.5289 (2)	0.3706 (1)	0.4776 (2)	0.0445 (6)
O3A	0.3235 (2)	0.3212 (1)	0.2361 (2)	0.0518 (7)
O4A	0.3495 (2)	0.1495 (1)	0.2224 (2)	0.0523 (7)
C1A	0.5619 (3)	0.2578 (2)	0.6002 (3)	0.050 (1)
C2A	0.6034 (3)	0.3438 (2)	0.6020 (3)	0.051 (1)
C3A	0.4203 (3)	0.4012 (2)	0.4956 (4)	0.055 (1)
C4A	0.3429 (3)	0.4050 (3)	0.3466 (4)	0.059 (1)
C5A	0.2254 (3)	0.2690 (3)	0.2323 (5)	0.077 (1)
C6A	0.2362 (3)	0.1786 (3)	0.1595 (4)	0.069 (1)
C7A	0.3605 (3)	0.1246 (2)	0.3532 (4)	0.060 (1)
C8A	0.4879 (3)	0.1179 (2)	0.4251 (4)	0.061 (1)
O1B†	0.6981 (4)	0.2693 (3)	0.3098 (5)	0.035 (1)
O2B†	0.5636 (4)	0.1187 (3)	0.1241 (5)	0.044 (1)

	x	y	z	U_{eq}/U_{iso}
O3B†	0.4290 (5)	0.2350 (4)	0.0008 (6)	0.048 (1)
O4B†	0.5636 (4)	0.3887 (3)	0.1870 (5)	0.050 (1)
C1B†	0.7475 (5)	0.1851 (4)	0.2972 (6)	0.042 (2)
C2B†	0.6884 (6)	0.1236 (3)	0.1469 (7)	0.050 (2)
C3B†	0.4906 (6)	0.0951 (3)	−0.0296 (6)	0.050 (2)
C4B†	0.4766 (5)	0.1688 (3)	−0.0926 (5)	0.053 (2)
C5B†	0.4176 (5)	0.3143 (5)	−0.0395 (7)	0.049 (2)
C6B†	0.5307 (5)	0.3703 (5)	0.0285 (6)	0.057 (2)
C7B†	0.6910 (5)	0.4030 (3)	0.2600 (7)	0.039 (2)
C8B†	0.7514 (4)	0.3216 (3)	0.2487 (5)	0.041 (1)
O1C‡	0.418 (1)	0.2045 (7)	−0.010 (2)	0.047 (4)
O2C‡	0.5172 (8)	0.3716 (7)	0.150 (1)	0.041 (3)
O3C‡	0.701 (1)	0.2988 (7)	0.316 (2)	0.043 (4)
O4C‡	0.603 (1)	0.1308 (8)	0.162 (1)	0.043 (4)
C1C‡	0.438 (1)	0.2595 (8)	−0.085 (1)	0.043 (3)
C2C‡	0.432 (2)	0.3547 (10)	0.007 (2)	0.055 (5)
C3C‡	0.635 (1)	0.3906 (7)	0.157 (1)	0.039 (3)
C4C‡	0.714 (1)	0.3821 (9)	0.307 (1)	0.036 (4)
C5C‡	0.7709 (9)	0.2355 (7)	0.253 (1)	0.038 (2)
C6C‡	0.723 (1)	0.146 (1)	0.240 (2)	0.045 (4)
C7C‡	0.576 (1)	0.1074 (6)	0.004 (1)	0.036 (2)
C8C‡	0.442 (1)	0.1170 (9)	−0.066 (1)	0.039 (3)
Li3	0.5005 (5)	0.2556 (4)	0.2523 (6)	0.047 (2)
C9A	0.0734 (2)	−0.0013 (2)	0.3103 (3)	0.0325 (8)
C10A	0.0808 (3)	0.0865 (2)	0.3961 (3)	0.0394 (9)
C11A	0.1637 (3)	0.0941 (2)	0.5378 (3)	0.0411 (9)
C12A	0.2097 (3)	0.0130 (2)	0.5397 (3)	0.0380 (9)
C13A	0.1514 (2)	−0.0462 (2)	0.3978 (3)	0.0307 (8)
C14A	0.1524 (3)	−0.1365 (2)	0.2967 (3)	0.0330 (8)
C15A	0.2174 (3)	−0.1281 (2)	0.1861 (3)	0.0403 (9)
C16A	0.1313 (3)	−0.0789 (2)	0.0884 (3)	0.0433 (10)
C17A	0.0264 (3)	−0.0638 (2)	0.1544 (3)	0.0397 (9)
C18A	0.0228 (3)	−0.1500 (2)	0.1921 (3)	0.0398 (9)
Li2	0	0	1/2	0.045 (2)
C9B	0.8699 (2)	0.5573 (2)	0.1283 (3)	0.0289 (8)
C10B	0.8016 (2)	0.4954 (2)	−0.0043 (3)	0.0360 (9)
C11B	0.8460 (3)	0.4140 (2)	0.0011 (3)	0.0412 (9)
C12B	0.9383 (3)	0.4251 (2)	0.1381 (4)	0.0408 (10)
C13B	0.9533 (2)	0.5146 (2)	0.2152 (3)	0.0319 (8)
C14B	1.0106 (3)	0.5812 (2)	0.3652 (3)	0.0396 (9)
C15B	0.9154 (3)	0.6012 (2)	0.4458 (3)	0.0448 (10)
C16B	0.8217 (3)	0.6469 (2)	0.3479 (3)	0.0401 (9)
C17B	0.8761 (3)	0.6499 (2)	0.2248 (3)	0.0338 (8)
C18B	1.0093 (3)	0.6637 (2)	0.3169 (3)	0.0409 (9)
Li1	1	1/2	0	0.040 (2)

† Occupancy = 0.69 (1).   ‡ Occupancy = 0.31 (1); U_{iso}.

Table 4. *Selected geometric parameters (Å, °) for (5)*

O1A—Li3	2.413 (6)	C13A—Li2	2.324 (2)
O2A—Li3	2.375 (6)	C14A—C15A	1.554 (4)
O3A—Li3	2.304 (6)	C14A—C18A	1.534 (4)
O4A—Li3	2.388 (6)	C15A—C16A	1.547 (4)
O1B—Li3	2.225 (7)	C16A—C17A	1.556 (4)
O2B—Li3	2.431 (7)	C17A—C18A	1.546 (4)
O3B—Li3	2.282 (7)	C9B—C10B	1.404 (4)
O4B—Li3	2.601 (7)	C9B—C13B	1.403 (4)
O1C—Li3	2.356 (16)	C9B—C17B	1.507 (4)
O2C—Li3	2.409 (12)	C9B—Li1	2.300 (2)
O3C—Li3	2.322 (15)	C10B—C11B	1.411 (4)
O4C—Li3	2.411 (15)	C10B—Li1	2.334 (3)
C9A—C10A	1.411 (4)	C11B—C12B	1.412 (4)
C9A—C13A	1.400 (4)	C11B—Li1	2.318 (3)
C9A—C17A	1.507 (4)	C12B—C13B	1.407 (4)
C9A—Li2	2.292 (3)	C12B—Li1	2.341 (3)
C10A—C11A	1.406 (4)	C13B—C14B	1.509 (4)
C10A—Li2	2.328 (3)	C13B—Li1	2.304 (3)
C11A—C12A	1.409 (4)	C14B—C15B	1.548 (4)
C11A—Li2	2.353 (3)	C14B—C18B	1.538 (4)
C12A—C13A	1.411 (4)	C15B—C16B	1.554 (4)
C12A—Li2	2.389 (3)	C16B—C17B	1.555 (4)
C13A—C14A	1.507 (4)	C17B—C18B	1.535 (4)
C10A—C9A—C13A	108.7 (3)	C10B—C9B—C13B	108.8 (2)
C10A—C9A—C17A	144.1 (3)	C10B—C9B—C17B	143.7 (3)

C13A—C9A—C17A	106.6 (2)	C13B—C9B—C17B	106.6 (2)
C9A—C10A—C11A	106.6 (2)	C9B—C10B—C11B	106.7 (2)
C10A—C11A—C12A	109.6 (3)	C10B—C11B—C12B	109.3 (3)
C11A—C12A—C13A	106.6 (3)	C11B—C12B—C13B	106.7 (2)
C9A—C13A—C12A	108.5 (2)	C9B—C13B—C12B	108.6 (3)
C9A—C13A—C14A	106.9 (2)	C9B—C13B—C14B	106.5 (2)
C12A—C13A—C14A	143.8 (3)	C12B—C13B—C14B	143.9 (3)
C13A—C14A—C15A	107.2 (2)	C13B—C14B—C15B	107.4 (2)
C13A—C14A—C18A	100.0 (2)	C13B—C14B—C18B	100.3 (2)
C15A—C14A—C18A	99.4 (2)	C15B—C14B—C18B	99.6 (2)
C14A—C15A—C16A	103.6 (2)	C14B—C15B—C16B	103.1 (2)
C15A—C16A—C17A	103.2 (2)	C15B—C16B—C17B	103.3 (2)
C9A—C17A—C16A	107.8 (2)	C9B—C17B—C16B	106.4 (2)
C9A—C17A—C18A	99.8 (2)	C9B—C17B—C18B	100.4 (2)
C16A—C17A—C18A	99.2 (2)	C16B—C17B—C18B	99.8 (2)
C14A—C18A—C17A	94.9 (2)	C14B—C18B—C17B	94.8 (2)

As seen in an earlier model for (4) (Zaegel *et al.*, 1994), the large anisotropic displacement parameters for the TMEDA ligand, in particular for C11 and C12, along with a short C11—C12 bond length of 1.312 (10) Å, indicate a disorder problem for this group with respect to the orientation of the ethylene bridge. This bridge was modeled here (*SHELXL*93; Sheldrick, 1993) with two sets of atoms: C11A—C12A and C11B—C12B, with occupancy factors of 0.40 (2) and 0.60 (2), respectively. These two bond lengths were restrained to be equal and all four atoms were refined isotropically. Several Li(TMEDA) structures in the literature exhibit this type of disorder: Li[C$_5$H$_4$Si(CH$_3$)$_3$]TMEDA (Lappert *et al.*, 1984), Li{C$_5$H$_2$[Si(CH$_3$)$_3$]$_3$}TMEDA (Jutzi *et al.*, 1985), (indenyl)Li(TMEDA) (Rhine & Stucky, 1975), (triphenylmethyl)Li(TMEDA) (Brooks & Stucky, 1972) and (naphthalenide)Li(TMEDA) (Brooks, Rhine & Stucky, 1972). H atoms were added to (4) at calculated positions and readjusted using a riding model. For each set of methyl group H atoms, a torsion angle was refined in order to determine the orientation of the H atoms about the methyl C atom (*AFIX*137 in *SHELXL*93).

The unit cell of (5) contains two independent [Li(isodiCp)$_2$]⁻ complexes and two [Li(12-crown-4)$_2$]⁺ ions. Two Li⁺ ions occupy symmetry inequivalent inversion centers (Li1 at 1,0.5,0 and Li2 at 0,0,0.5) and each is coordinated by two isodiCp ligands. There is a third Li⁺ ion, Li3, at a general position and it is coordinated by two 12-crown-4 molecules, labeled as *A* and *B*. Crown *B* is disordered in that it exists in an alternate orientation, labeled as crown *C*. The atoms for crown *C*, readily apparent on a difference electron-density map, were refined only isotropically. The occupancy factor, α, for crown *B* refined to 0.69 (1). Since the occupancy factor for crown *C* was constrained to be $1 - \alpha$, its final value was 0.31 (1). H atoms were included in the model at calculated positions.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993) for (4); *TEXSAN* for (5). For both compounds, molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a unit-cell diagram of structure (5), have been deposited with the IUCr (Reference: BK1216). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bauer, W., O'Doherty, G. A., Schleyer, P. von R. & Paquette, L. A. (1991). *J. Am. Chem. Soc.* **113**, 7093–7100.

Bauer, W., Sivik, M. R., Friedrich, D., Schleyer, P. von R. & Paquette, L. A. (1992). *Organometallics*, **11**, 4178–4189.

Brooks, J. J. & Stucky, G. D. (1972). *J. Am. Chem. Soc.* **94**, 7333–7338.

Brooks, J. J., Rhine, W. & Stucky, G. D. (1972). *J. Am. Chem. Soc.* **94**, 7346–7351.

Chen, H., Jutzi, P., Leffers, W., Olmstead, M. M. & Power, P. P. (1991). *Organometallics*, **10**, 1282–1286.

Gallucci, J. C., Gautheron, B., Gugelchuk, M., Meunier, P. & Paquette, L. A. (1987). *Organometallics*, **6**, 15–19.

Hammel, A., Schwarz, W. & Weidlein, J. (1990). *Acta Cryst.* C**46**, 2337–2339.

Hope, H. (1987). *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*. Am. Chem. Soc. Symp. Ser. No. 357, edited by A. L. Wayda & M. Y. Darensbourg, pp. 257–262. Washington, DC: American Chemical Society.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jutzi, P., Schlüter, E., Krüger, C. & Pohl, S. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 994.

Jutzi, P., Schlüter, E., Pohl, S. & Saak, W. (1985). *Chem. Ber.* **118**, 1959–1967.

Lappert, M. F., Singh, A., Engelhardt, L. M. & White, A. H. (1984). *J. Organomet. Chem.* **262**, 271–278.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Moriarty, K. J., Rogers, R. D. & Paquette L. A. (1989). *Organometallics*, **8**, 1512–1517.

Paquette, L. A., Bauer, W., Sivik, M. R., Bühl, M., Feigel, M. & Schleyer, P. von R. (1990). *J. Am. Chem. Soc.* **112**, 8776–8789.

Paquette, L. A., Charumilind, P. & Gallucci, J. C. (1983). *J. Am. Chem. Soc.* **105**, 7364–7373.

Paquette, L. A., Charumilind, P., Kravetz, T. M., Böhm, M. C. & Gleiter, R. (1983). *J. Am. Chem. Soc.* **105**, 3126–3135.

Paquette, L. A., Moriarty, K. J., McKinney, J. A. & Rogers, R. D. (1989). *Organometallics*, **8**, 1707–1713.

Paquette, L. A., Moriarty, K. J., Meunier, P., Gautheron, B. & Crocq, V. (1988). *Organometallics*, **7**, 1873–1875.

Paquette, L. A., Moriarty, K. J., Meunier, P., Gautheron, B., Sornay, C., Rogers, R. D. & Rheingold, A. L. (1989). *Organometallics*, **8**, 2159–2167.

Paquette, L. A., Moriarty, K. J. & Rogers, R. D. (1989). *Organometallics*, **8**, 1506–1511.

Paquette, L. A. & Sivik, M. R. (1992). *Organometallics*, **11**, 3503–3505.

Paquette, L. A., Sivik, M. R., Bauer, W. & Schleyer, P. von R. (1994). *Organometallics*, **13**, 4919–4927.

Power, P. P. (1988). *Acc. Chem. Res.* **21**, 147–153.

Rhine, W. E. & Stucky, G. D. (1975). *J. Am. Chem. Soc.* **97**, 737–743.

Rogers, R. D., Sivik, M. R. & Paquette, L. A. (1993). *J. Organomet. Chem.* **450**, 125–135.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sivik, M. R., Rogers, R. D. & Paquette, L. A. (1990). *J. Organomet. Chem.* **397**, 177–185.

Sornay, C., Meunier, P., Gautheron, B., O'Doherty, G. A. & Paquette, L. A. (1991). *Organometallics*, **10**, 2082–2083.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zaegel, F., Gallucci, J. C., Meunier, P., Gautheron, B., Sivik, M. R. & Paquette, L. A. (1994). *J. Am. Chem. Soc.* **116**, 6466–6467.

(I)

Aqua(hexacyanoferrato-*N*)bis(μ-glycine)-glycinecerium(III) Monohydrate

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Abstract

The structure of the title compound, [Ce{Fe(CN)$_6$}-(C$_2$H$_5$NO$_2$)$_3$(H$_2$O)].H$_2$O, consists of FeC$_6$ octahedra linked to an eight-coordinate cerium ion *via* two cyanide bridging Ce—N—C—Fe groups. The rest of the coordination polyhedron of the cerium is formed by six O atoms: one from a molecule of water and five from glycine molecules. The three-dimensional framework is formed through N—H$\cdots$N and O—H$\cdots$N hydrogen-bonding interactions. Two glycine molecules form bifurcated hydrogen bonds. An additional uncoordinated molecule of water is within hydrogen-bonding distance of two glycine molecules.

Comment

In a previous paper, we reported the synthesis and the characterization, by X-ray powder diffraction, thermal analysis and Mössbauer and IR spectroscopy, of the hexacyanocobaltate(III) and the hexacyanoferrate(III) of lanthanum and glycine (Fernández-Bertrán, Reguera, Dago & López, 1996). We found that glycine takes the neutral zwitterion form. As a continuation of our studies of the metal–ligand bond interactions in this type of complex, the crystal structure of the isotypic cerium analogue, (I), was determined.
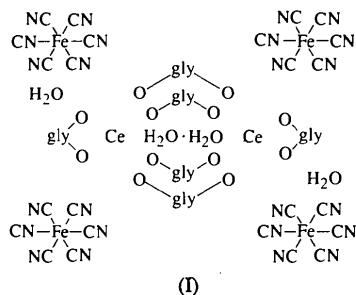
The low spin Fe^{3+} ion is octahedrally coordinated to six cyano groups. The average Fe—C and C—N bond distances are 1.941 (3) and 1.143 (4) Å, respectively, which compare well with literature values (Mullica, Herbert, Sappenfield & David, 1988). The Ce^{3+} ion is eight-coordinate. This is fairly common in molecular complexes of the lanthanide series (Hulliger, Landolt & Vetsch, 1976). Only two cyano groups are coordinated to cerium (Ce—N1 and Ce—N2), which is in accordance with IR and Mössbauer results (Fernández-Bertrán *et al.*, 1996), with an average Ce—N bond length of 2.623 (3) Å. The rest of the coordination polyhedron is formed by six O atoms, one from water (O7) and five from glycine moieties. The average Ce—O bond length is 2.502 (2) Å. The structure consists of FeC$_6$ octahedra linked to cerium *via* two cyanide bridging Ce—N—C—Fe linkages. The three-dimensional framework is completed through hydrogen-bonding interactions (Table 3). Among these, the most significant are the N—H$\cdots$N interactions that link glycine NH$_3$ groups with the N atoms of the cyano groups not bonded to the Ce ion. The uncoordinated O atom of the glycine (O6) forms three hydrogen bonds, of which two are strong (to the water molecule coordinated to the cerium ion, O7—
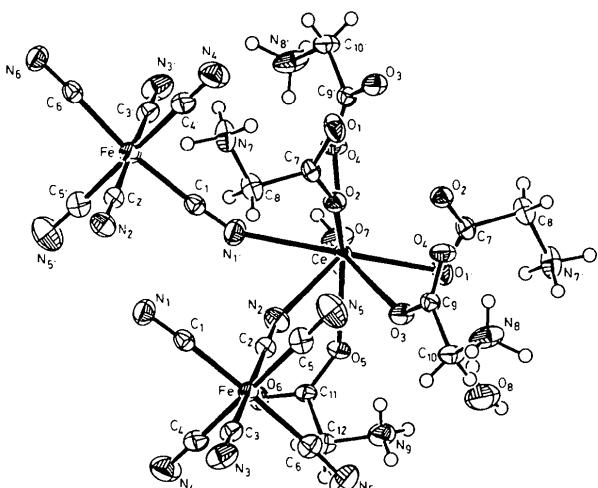

Fig. 1. *EUCLID* (Spek, 1982) plot, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are represented by spheres of arbitrary radii.