

## A Novel Bonding Mode of Oximate Ligand to a Metal; Synthesis and X-Ray Crystal Structure of Bis[acetone oximatobis(cyclopentadienyl)gadolinium] $[(C_5H_5)_2Gd(\mu-\eta^2-ONCMe_2)]_2$

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Reaction of  $[Cp_3Gd]$  ( $Cp = C_5H_5$ ) with acetone oxime in THF at room temp. results in the formation of a new complex  $[(Cp_2Gd(\mu-\eta^2-ONCMe_2))]_2$ ; X-ray analysis shows an unusual structure with the O–N fragment of  $ONCMe_2$  ligand acting as both a bridging and side-on donating group.

The oxime group is an unusual ligand because of the many different ways in which it can be bind to a metal ion. King *et al.*<sup>1</sup> suggested at least four possible modes for the binding of the  $ONCMe_2$  ligand to a metal, including binding through C and N, C and O, and N and O or *via* a delocalized  $\pi$  system involving C, N and O. Structural studies on metal oximate complexes, however, are based mainly on spectroscopic data and the conclusions derived are mostly tentative. Up till now, only structures containing a metal–N–O–metal bridge<sup>2</sup> and side-on chelating O–N group<sup>3,4b</sup> have been confirmed by crystallographic studies. To date, much has been published on transition-metal complexes involving oxime groups, due to the interest in the structures and properties of these complexes.<sup>5</sup> Nevertheless, the syntheses and studies on organometallic oximate complexes (especially on organolanthanides) are relatively rare.<sup>4</sup> Lanthanide ions are large and can accommodate high coordination numbers, 8–12, and as a result form ligand-bridging polynuclear structural complexes. In order to investigate the bonding mode of oximate ligand to lanthanide ions, we report herein the first X-ray crystal structure of the organolanthanide oximate complex  $[(Cp_2Gd(\mu-\eta^2-ONCMe_2))]_2$ .

The complex was synthesized as follows:† to a 20 ml THF solution of  $[Cp_3Gd]$  (1.5 mmol), an equimolar amount of  $HONCMe_2$  in 10 ml THF was added dropwise with stirring. The reaction mixture was stirred overnight at room temp. and then concentrated under reduced pressure to *ca.* 10 ml to give a white precipitate, which was filtered off, washed twice with *n*-hexane and dried *in vacuo* in 56.3% yield. Crystals suitable for X-ray analysis were obtained by cooling the hot saturated THF solution of the complex to room temp.

The complex has been characterized by elemental analysis, IR and MS spectra,‡ and by X-ray crystallography.§ The IR spectra exhibit the characteristic absorptions for the  $\eta^5$ -Cp ligand.<sup>6</sup> The band at  $472\text{ cm}^{-1}$  may be assigned to the  $\nu(Ln-O)$  stretching.<sup>7</sup> The  $\nu(C=N)$  frequency in the IR spectra of the complex is  $38\text{ cm}^{-1}$  lower than the corresponding value ( $1678\text{ cm}^{-1}$ ) of the parent acetoxime, suggesting coordination through a nitrogen atom.<sup>8</sup> An absorption peak at  $393\text{ cm}^{-1}$  may be attributed to the  $\nu(Ln-N)$  stretching.<sup>9</sup> The mass spectrum of the complex displays a series of peaks representing clearly the fragments derived from the dimer  $[(Cp_2Gd(ONCMe_2))]_2$ , although the molecular-ion peaks were not observed. The fragment formed by loss of a Cp group from the dimer was revealed by a peak at  $m/z = 655$ . The peaks corresponding to the  $[CpGd_2O]^+$  and  $[Gd_2O_2]^+$  ions evidently indicate the oxygen-bridging structure of the complex.

The structure (Fig. 1) shows that the molecule is asymmetric and has a typical bent sandwich metallocene structure. X-Ray analysis has revealed an unusual bonding mode of the  $ONCMe_2$  ligand, and that the O–N fragment of the oximate group acts as both a bridging and side-on donating ligand. The gadolinium atom is coordinated by two cyclopentadienyl ring centroids, two oxygen atoms and one nitrogen atom of the acetoximate ligands leading to a distorted trigonal-bipyrami-

dal geometry with oxygen and nitrogen atoms in axial positions, with the metal nine-coordinate if the Cp group is viewed as occupying three coordination sites. The most interesting part of the structure is the acetoximate bridge which connects the two  $Cp_2Gd$  moieties. The six atoms comprising the N–OGd<sub>2</sub>O–N unit are nearly planar. The  $Gd_2N_2$  unit forms a near-parallelogram which contains the rhombic quadrilateral unit  $Gd_2O_2$ .

The Gd–C(Cp) distances range from 2.56(2) to 2.75(2) Å and average 2.68(2) Å, and are similar to those reported for related complexes:  $[CpGdCl_2]\cdot 3THF$ , 2.683(6) Å;<sup>10</sup>  $[Cp_2GdCl]_4$ , 2.67(4) Å.<sup>11</sup> The Gd–O bond lengths can be divided into two sets, namely, Gd(1)–O(1) 2.25(1), Gd(2)–O(2) 2.29(1) Å, and Gd(1)–O(2) 2.38(1), Gd(2)–O(1) 2.37(1) Å. It is obvious that the bond lengths in the former set are significantly shorter than the latter. Nevertheless, the Ln–O bond distances reported for some known oxygen-bridging complexes containing  $Cp_2Ln$  units are usually similar.<sup>12</sup> Thus, the large Gd–O bond lengths in the structure may be indicative of donor Gd–O interactions, and are close to the Gd–O(THF) bond length [2.397(3) Å] in  $[CpGdCl_2]\cdot 3THF$ .<sup>10</sup> This can be verified by the known complex  $[(Cp_2Yb[\mu-OCH(Me)CO_2Bu^i])_2]$ , which contains both bridging and intramolecular coordination Yb–O bonds.<sup>12f</sup> The Gd–N distance [2.42(1) Å] is longer than those found in the

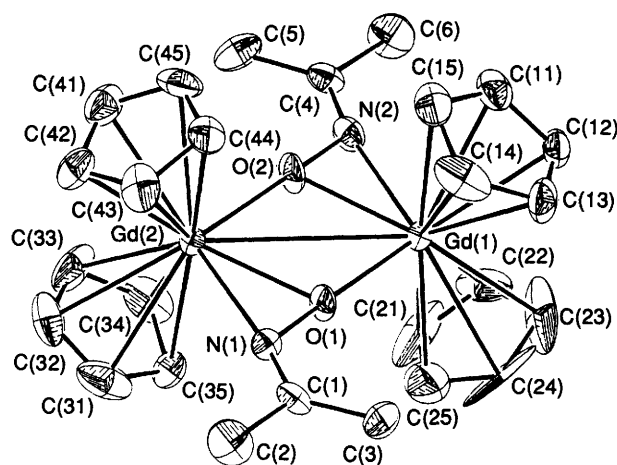


Fig. 1 Molecular structure and atom numbering scheme for  $[(Cp_2Gd(\mu-\eta^2-ONCMe_2))]_2$ . Selected bond distances (Å) and angles ( $^\circ$ ): Gd(1)–O(1) 2.25(1), Gd(1)–O(2) 2.38(1), Gd(2)–O(1) 2.37(1), Gd(2)–O(2) 2.29(1), Gd(1)–N(2) 2.40(1), Gd(2)–N(1) 2.43(1), Gd(1)–Gd(2) 3.718(2), N(1)–O(1), 1.38(2), N(2)–O(2) 1.34(2), C(1)–N(1) 1.26(2), C(4)–N(2) 1.27(2), Gd(1)–Cp(1) 2.415, Gd(1)–Cp(2) 2.373, Gd(2)–Cp(3) 2.452, Gd(2)–Cp(4) 2.438; Gd(1)–O(1)–Gd(2) 107.2(4), Gd(1)–O(2)–Gd(2) 105.6(4), O(1)–Gd(1)–O(2) 73.9(3), O(1)–Gd(2)–O(2) 73.3(3), Gd(1)–O(1)–N(1), 176.4(8), Gd(2)–O(2)–N(2) 179(1), Gd(1)–N(2)–O(2) 72.8(7), Gd(2)–N(1)–O(1) 70.8(6), O(1)–N(1)–C(1) 118(1), O(2)–N(2)–C(4) 119(2), Cp(1)–Gd(1)–Cp(2) 127.37, Cp(3)–Gd(2)–Cp(4) 126.49 (Cp = centroid of cyclopentadienyl ring).

structurally similar complexes  $[\{\text{Cp}_2\text{Ln}(\mu\text{-}\eta^2\text{-HC=NCMe}_3)_2\}]$  (Ln = Y,<sup>13a</sup> Er<sup>13b</sup>), which can be accounted for by the difference in metallic ion radii.

The C–N [1.26(1) Å] and N–O [1.36(2) Å] distances in the ONCMe<sub>2</sub> ligand are consistent with the description of these bonds as a double and a single bond, respectively, and are close to those reported for HONCMe<sub>2</sub>.<sup>14</sup> The O–N–C angle [118(1)°] is similar to those found in other bridging oximate ligands<sup>2</sup> and is smaller than those in the chelating ligands,<sup>3,4b</sup> despite the bridging and chelating features of the acetoximate ligand in the title complex. It is interesting to note that the Gd(1)–O(1)–N(1) [176.4(8)°] and Gd(2)–O(2)–N(2) [179(1)°] angles both are near 180°. It is evident that this near-linear configuration is most reasonable for the structure and is favourable for the O–N fragment of the oximate ligand coordinated to the second Gd atom in an  $\eta^2$  fashion. The Cp–Gd–Cp angle (126.9°) is similar to those found in related complexes:  $[\{\text{Cp}_2\text{Yb}(\text{OC}_3\text{H}_3)_2\}]$  126.3°,<sup>12c</sup>  $[\{\text{Cp}_2\text{Lu}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$ , 127.2°. It is, however, smaller than that found in  $[\{\text{Cp}_2\text{Y}(\text{OH})_2\}]$ , 130.1°.<sup>12a</sup> Evidently, this variation in angles results from the larger steric bulk of the bridging ligand in the former complex than the latter.

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### Footnotes

† All manipulations were performed under a moisture- and oxygen-free argon atmosphere or in a glovebox.

‡ Selected spectroscopic data: IR (Nujol and Fluoroluble mulls):  $\nu/\text{cm}^{-1}$  3071w, 2923s, 2852s, 1640w, 1462s, 1445s, 1378s, 1262m, 1012s, 991s, 782s, 768s, 639s, 472m, 393s, 242s. MS (EI mode; <sup>12</sup>C, <sup>1</sup>H, <sup>14</sup>N, <sup>16</sup>O and <sup>158</sup>Gd): *m/z* (fragment, relative intensity %) 655 (M – Cp, 69.1), 590 (M – 2Cp, 4.5), 575 (M – 2Cp – Me, 15.1), 534 (M – 2Cp – NCMe<sub>2</sub>, 36.8), 519 (M – 2Cp – NCMe<sub>2</sub> – Me, 4.7), 478 (M – 2Cp – 2NCMe<sub>2</sub>, 5.5), 469 (M – 3Cp – NCMe<sub>2</sub>, 5.3), 454 (M – 3Cp – NCMe<sub>2</sub> – Me, 5.4), 413 (M – 3Cp – 2NCMe<sub>2</sub>, 30.7), 397 (CpGd<sub>2</sub>O, 3.4), 348 (Gd<sub>2</sub>O<sub>2</sub>, 5.2), 295 (M/2 – Cp, 4.0), 288 (M/2 – ONCMe<sub>2</sub>, 10.4), 223 (M/2 – Cp – ONCMe<sub>2</sub>, 4.2), 215 (M/2 – 2Cp – Me, 5.3), 174 (GdO, 5.4), 73 (HONCMe<sub>2</sub>, 4.1), 72 (ONCMe<sub>2</sub>, 3.4), 66 (HCp, 100.0), 65 (Cp, 59.9), 56 (NCMe<sub>2</sub>, 3.8), 41 (NCMe, 40.0), satisfactory elemental analyses were obtained.

§ Crystal data for  $[\{\text{Cp}_2\text{Gd}(\text{ONCMe}_2)_2\}]$ , *M* = 719.1, orthorhombic, space group *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub>, *a* = 8.136(3), *b* = 15.807(7), *c* = 20.508(7) Å, *V* = 2637(2) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.81 g cm<sup>-3</sup>, *F*(000) = 1384,  $\mu$  = 50.3 cm<sup>-1</sup>, *R* = 0.041, *R<sub>w</sub>* = 0.049, GOF = 1.31, weighting scheme 1/ $\sigma^2(F_o)$ ,  $\Delta\rho_{\text{min}}$  = –0.778 e Å<sup>-3</sup>,  $\Delta\rho_{\text{max}}$  = 0.831 e Å<sup>-3</sup>. Data were collected on an Enraf-Nonius CAD4 diffractometer at room temp., using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71069 Å). The polar direction of the space group was not established. Scan type  $\omega$ –2 $\theta$ , 2 $\theta_{\text{max}}$  = 49.9°. 2324 Unique reflections with *I* ≥ 3 $\sigma$ (*I*) were used in the refinement. The intensities were corrected for Lorentz-polarization effects and empirically for absorption. The structure was

solved by direct methods and Fourier synthesis. All non-hydrogen atoms were refined anisotropically by the least-squares method. The hydrogen atoms were added at calculated positions using a C–H bond length of 0.95 Å and ideal bond angles, and were included in the structure-factor calculation. All calculations were performed on a MICRO VAX 3100 computer using MSC/Rigaku TEXSAN programme. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

### References

- 1 R. B. King and W. M. Douglass, *Inorg. Chem.*, 1974, **13**, 1339.
- 2 (a) G. P. Khare and R. J. Doedens, *Inorg. Chem.*, 1976, **15**, 86; (b) S. Aime, G. Gervasio, L. Milone, R. Rossetti and P. L. Stanghellini, *J. Chem. Soc., Chem. Commun.*, 1976, 370.
- 3 G. P. Khare and R. J. Doedens, *Inorg. Chem.*, 1977, **16**, 907.
- 4 (a) A. Singh, V. D. Gupta, G. Srivastava and R. C. Mehrotra, *J. Organomet. Chem.*, 1974, **64**, 145 and references cited therein; (b) U. Thewlt and R. Friedrich, *Z. Naturforsch., Teil B: Chem. Sci.*, 1991, **46**, 475; (c) X. Wang, X. Shen and B. Duo, *Polyhedron*, 1992, **11**, 335; *Synth. React. Inorg. Met.-Org. Chem.*, 1993, **23**, 419.
- 5 (a) A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1 and references cited therein; (b) R. C. Mehrotra, A. K. Rai, A. Singh and R. Bohra, *Inorg. Chim. Acta*, 1975, **13**, 91; (c) M. E. Keeney, K. Osseo-Asake and K. A. Woode, *Coord. Chem. Rev.*, 1984, **59**, 141; (d) R. P. Singh and N. K. Singh, *Asia J. Chem. Rev.*, 1991, **2**, 62.
- 6 (a) N. M. Ely and M. Tsutsui, *Inorg. Chem.*, 1975, **14**, 2680; (b) C. Qian, C. Ye, H. Lu, J. Zhou, Y. Ge and M. Tsutsui, *J. Organomet. Chem.*, 1983, **247**, 161.
- 7 (a) R. C. Mehrotra and J. M. Batwara, *Inorg. Chem.*, 1970, **9**, 2505; (b) L. M. Brown and K. S. Mazdiyashi, *Inorg. Chem.*, 1970, **9**, 2783.
- 8 J. R. Jennings and K. Wade, *J. Chem. Soc. A*, 1967, 1333.
- 9 Z. Wu, Z. Xu, X. You and X. Zhou, *Synth. React. Inorg. Met.-Org. Chem.*, 1993, **23**, 1155.
- 10 Z. Wu, Z. Xu, X. You, X. Zhou and L. Shi, *J. Coord. Chem.*, 1992, **26**, 329.
- 11 W. Lamberts, B. Hessner and H. Lueken, *Inorg. Chem. Acta*, 1987, **139**, 215.
- 12 (a) E. C. Baker, L. D. Brown and K. N. Raymond, *Inorg. Chem.*, 1975, **14**, 1376; (b) W. J. Evans, R. Dominguez and T. P. Hanusa, *Organometallics*, 1986, **5**, 1291; (c) Z. Wu, Z. Xu, X. You, X. Zhou, Y. Xing and Z. Jin, *J. Chem. Soc., Chem. Commun.*, 1993, 1495; (d) S. D. Stults, R. A. Anderson and A. Zalkin, *Organometallics*, 1990, **9**, 115; (e) G. Massarweh and R. D. Fischer, *J. Organomet. Chem.*, 1993, **444**, 67; (f) J. Stehr and R. D. Fischer, *J. Organomet. Chem.*, 1993, **459**, 79.
- 13 (a) W. J. Evans, J. H. Meadows, W. E. Hunter and J. L. Atwood, *Organometallics*, 1983, **2**, 1252; (b) W. J. Evans, T. P. Hanusa, J. H. Meadows, W. E. Hunter and J. L. Atwood, *Organometallics*, 1987, **6**, 295.
- 14 T. K. Bierlein and E. C. Lingafelter, *Acta Crystallogr.*, 1951, **4**, 450.
- 15 H. Schumann, E. Palamidis and J. Loebel, *J. Organomet. Chem.*, 1990, **384**, C49.