Acta Cryst. (1988). C**44**, 433–435

An *N,N'*-Hydrazonide Metal Complex: The Crystal Structure of Bis(pentamethylcyclopentadienyl)[η^2-bis(*p*-tolyl) ketone methylhydrazonido]hydroxozirconium†

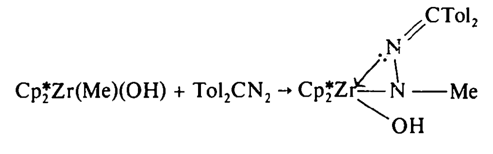
By B. D. Santarsiero‡ and E. J. Moore

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

(*Received* 17 *November* 1986; *accepted* 14 *October* 1987)

Abstract. [Zr($C_{10}H_{15}$)$_2$($C_{16}H_{17}N_2$)(OH)], $M_r = 616{\cdot}02$, monoclinic, $P2_1/n$, $a = 10{\cdot}935$ (3), $b = 20{\cdot}557$ (6), $c = 14{\cdot}777$ (3) Å, $\beta = 90{\cdot}09$ (2)°, $V = 3321{\cdot}7$ (15) Å^3, $Z = 4$, $D_x = 1{\cdot}23$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $T \approx 290$ K, $\mu = 3{\cdot}52$ cm^{-1}, $F(000) = 1304$, S (goodness-of-fit) = 1·94 (6116 reflections), $R = 0{\cdot}080$ for the 5546 reflections with $I > 0$ and 0·051 for the 3798 reflections with $I > 3\sigma$. The *N'*-methylbis(*p*-tolyl)diazomethane group is coordinated to the Zr atom by a σ bond [Zr—N, 2·112 (4) Å] to the methylated N atom and by a dative bond [2·348 (4) Å] from the di(*p*-tolyl)methyl N atom.

Introduction. In an effort to explore the reactivity of diazo reagents with bis(pentamethylcyclopentadienyl)zirconium(IV) complexes, the monoalkyl Cp$^*_2$Zr(Me)(OH) complex (Me ≡ CH_3, Cp* ≡ C_5Me_5) was treated with one equivalent of bis(*p*-tolyl)diazomethane, Tol_2CN_2 (Tol ≡ C_6H_4Me), at 333 K to generate the η^2-*N,N'*-hydroxohydrazonide metal complex Cp$^*_2$Zr(NMeNCTol$_2$)OH (Moore, 1984), with Zr—N bonds to both N atoms.



Experimental. The complex can be isolated as a lemon-colored solid in 47% yield by recrystallization from petroleum ether. The ^{1}H NMR spectrum displays a single resonance at δ 1·90 for the η^5-Cp* protons, a resonance at δ 2·86 for the NCH_3 protons, and resonances characteristic of two inequivalent tolyl ligands. The presence of the hydroxyl ligand is confirmed by an OH proton at δ 2·60 and an O—H stretch at 3695 cm^{-1} in the IR spectrum.

Yellow crystals from benzene, air-sensitive. Specimen, 0·30 × 0·35 × 0·70 mm, sealed in glass capillary under N_2. Space group $P2_1/n$ from oscillation and Weissenberg photographs (systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd). Diffractometry: Syntex $P2_1$, graphite monochromator, Mo $K\alpha$ radiation. Lattice constants by least-squares constrained ($\alpha = \gamma = 90°$) refinement of 29 average 2θ values ($\pm 2\theta$ for each reflection, $20 < 2\theta < 36°$). Intensity measurements: 7664 reflections ($+h$, $+k$, $\pm l$), $2\theta < 56°$, θ–2θ scans at 3·91° min^{-1} with 2θ width 2·2° plus angular dispersion; scan-to-background time ratio $r = t_s/t_b = 2{\cdot}0$; stationary-counter–stationary-crystal background counts fore and aft. Three check reflections, every 97 reflections – no decomposition. No absorption correction, data averaged over $2/m$ symmetry, preliminary scaling by Wilson (1942) plot. Structure derivation: Patterson and electron density maps. Refinement: full-matrix least squares on F^2, all reflections, weights w, $w^{-1} = [s + r^2b + (0{\cdot}02s)^2]k^4/(Lp)^2$ (s = scan counts, b = total background counts, k = scale factor), anisotropic Gaussian amplitudes, atomic form factors from *International Tables for X-ray Crystallography* (1974), including f' and f'' for Zr.

The coordinates of H atoms were determined from difference maps, and were not refined. *CRYM* program library (Duchamp, 1964); final S (goodness-of-fit) = 1·94 (6616 total, averaged reflections, 361 parameters), $R = 0{\cdot}080$ (5546 reflections, $I > 0$), $R' = 0{\cdot}051$ (3798 reflections, $I > 3\sigma$), maximum peak 0·7 e Å^{-3} in final ΔF map, mean and maximum ratio of shift/e.s.d. in final cycle: 0·05 and 0·10.

Discussion. The coordinates and U's are given in Table 1, with important bond lengths and angles given in Fig. 1, and a molecular view in Fig. 2.§ The Cp* rings are coordinated to the Zr atom in the typical pentahapto fashion, and three atoms coordinate to the metal in the

---

† Contribution No. 7505 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA.

‡ Myron A. Bantrell Fellow 1981–1983. Present address: Department of Biochemistry, 474 Medical Sciences Building, University of Alberta, Edmonton, AB, T6G 2H7, Canada.

§ Fractional atom coordinates for H atoms, anisotropic Gaussian amplitudes for non-hydrogen atoms, complete listing of bond lengths and angles, least-squares-plane information, and a listing of structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44459 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/88/030433-03$03.00

Table 1. *Atom coordinates* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^4$)

	x	*y*	*z*	U_{eq}(Å^2)
Zr	9407·8 (4)	2230·2 (2)	465·0 (3)	322 (1)
O	10982 (3)	1632 (1)	1434 (2)	393 (7)
N(1)	9073 (3)	3295 (2)	984 (2)	368 (9)
N(2)	9844 (4)	2922 (2)	1473 (2)	436 (10)
C(1)	8745 (4)	3905 (2)	1100 (3)	373 (11)
C(2)	10346 (6)	3083 (3)	2345 (4)	701 (16)
C(11)	11319 (4)	2655 (2)	−394 (3)	445 (12)
C(12)	11256 (5)	1979 (2)	−594 (3)	443 (12)
C(13)	10223 (5)	1865 (2)	−1112 (3)	414 (12)
C(14)	9607 (5)	2465 (2)	−1240 (3)	433 (12)
C(15)	10319 (5)	2943 (2)	−822 (3)	448 (12)
C(21)	12331 (5)	2992 (3)	101 (4)	711 (16)
C(22)	12287 (6)	1506 (3)	−447 (4)	743 (17)
C(23)	10013 (6)	1238 (3)	−1639 (4)	696 (16)
C(24)	8588 (6)	2588 (3)	−1891 (3)	703 (17)
C(25)	10167 (6)	3676 (3)	−940 (4)	734 (17)
C(31)	7311 (5)	2104 (2)	1286 (3)	696 (16)
C(32)	8056 (5)	1603 (3)	1601 (3)	703 (17)
C(33)	8269 (5)	1173 (2)	878 (4)	734 (17)
C(34)	7629 (5)	1399 (3)	131 (3)	512 (13)
C(35)	7056 (5)	1991 (3)	360 (4)	520 (14)
C(41)	6763 (6)	2630 (3)	1847 (4)	531 (14)
C(42)	8384 (6)	1503 (4)	2572 (4)	559 (14)
C(43)	8880 (7)	521 (3)	925 (5)	538 (14)
C(44)	7311 (6)	1007 (3)	−716 (4)	875 (19)
C(45)	6054 (6)	2292 (3)	−194 (4)	940 (22)
C(51)	7862 (4)	4183 (2)	458 (3)	954 (24)
C(52)	7271 (6)	3829 (3)	−193 (4)	966 (21)
C(53)	6505 (6)	4107 (3)	−817 (4)	848 (19)
C(54)	6283 (5)	4771 (3)	−823 (4)	404 (11)
C(55)	6832 (5)	5127 (2)	−175 (4)	602 (16)
C(56)	7614 (5)	4852 (2)	464 (4)	534 (14)
C(57)	5485 (6)	5093 (3)	−1535 (4)	845 (19)
C(61)	9269 (5)	4338 (2)	1805 (3)	391 (11)
C(62)	10422 (5)	4600 (3)	1711 (3)	552 (14)
C(63)	10894 (5)	5031 (3)	2340 (4)	587 (15)
C(64)	10228 (6)	5220 (2)	3076 (4)	548 (14)
C(65)	9083 (6)	4961 (3)	3169 (4)	736 (17)
C(66)	8593 (5)	4535 (3)	2543 (4)	617 (15)
C(67)	10719 (7)	5702 (3)	3760 (4)	925 (21)

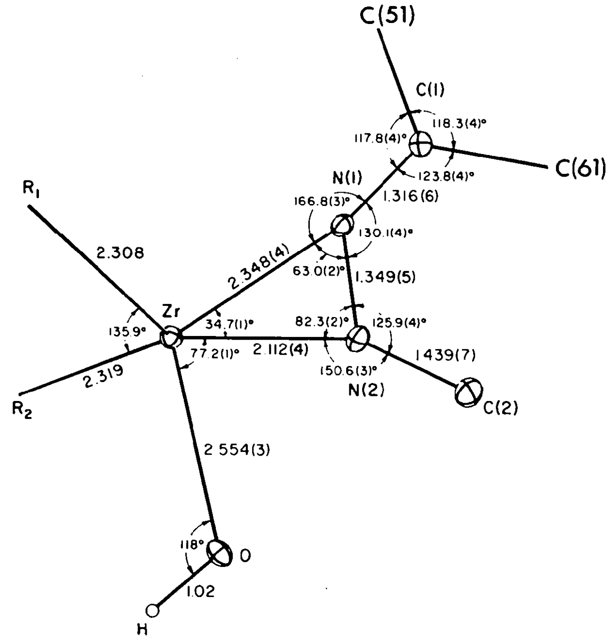


Fig. 1. Skeletal view of molecule with selected bond lengths (Å) and angles (°).

equatorial wedge, O and N(1) at lateral positions and N(2) at a central site.

The structure is quite similar to that of $Cp_2Zr(Me)NMeNC(C_6H_5)_2$ (Gambrotta, Bassobert, Floriani & Guastini, 1982; hereinafter GBFG), which was formed in an analogous manner but has a CH_3 rather than OH in the Zr coordination sphere. The Zr—N(1), 2·348 (4) Å, and Zr—N(2), 2·112 (4) Å, bond lengths are similar to those observed for GBFG [Zr—N(1), 2·283 (3), Zr—N(2), 2·103 (3) Å]. In both cases, the Zr—N(central) bond length is shorter than the Zr—N(lateral) bond length, implying a stronger bonding interaction between the Zr and central N atoms. The Zr—N(2) bond length is expected to be shorter than the Zr—N(1) bond length since the former bond results from a σ interaction and the latter from a dative interaction. A purely dative Zr—N interaction has been observed in the Zr–ketene compound $Cp^*_2Zr(OCCH_2)$(pyridine), which exhibits a Zr—N bond length of 2·403 (1) Å (Moore, Straus, Armantrout, Santarsiero, Grubbs & Bercaw, 1983). The N(1)—C(1) bond length of 1·316 (6) Å [*cf.* 1·307 (4) Å, GBFG] is characteristic of an N=C double bond (~ 1·30 Å, Dunitz, 1979), but the N(1)—N(2) bond length of 1·349 (5) Å [*cf.* 1·338 (4) Å, GBFG] is intermediate between an N—N single (1·45 Å, Dunitz, 1979), and an N=N double bond [1·25 Å (Dunitz, 1979); 1·238 Å, HN=NH (Trombetti, 1978); 1·254 Å, MeN=NMe (Chang, Porter & Bauer, 1970); and 1·244 Å, PhN=NPh (Brown, 1966)], and implies some electronic delocalization over the C—N—N unit. Thus, the hydrazonido group can be formulated (*p*-tolyl)$_2$C=N—N—CH_3. The N(2)—C(2) bond length is unexceptional: 1·439 (7) Å [*cf.* 1·446 (6) Å, GBFG]. The Zr, O, H, N(1), N(2), and C(1) atoms are all approximately coplanar with the greatest deviation from planarity observed for the N(2) (0·091 Å) and H (0·087 Å) atoms. The Zr—O bond length of 2·554 (3) Å is the longest reported to date [*cf.* 2·446 Å in $(COT)_2Zr.THF$ (Brauer & Kruger, 1972)]. Typical Zr—O bond lengths for complexes with a Zr—O σ interaction are 2·1–2·3 Å (*e.g.*, Fachinetti, Floriani,

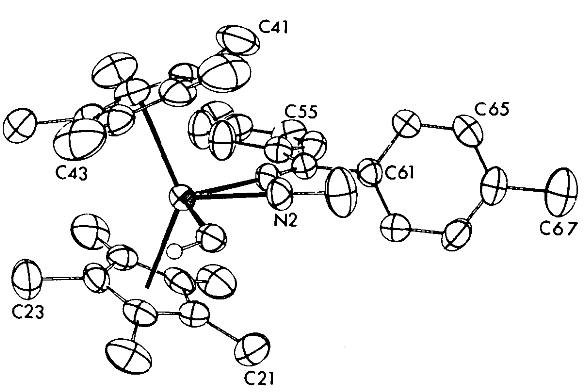


Fig. 2. Molecular view with atom labels.

Marchetti & Merlino, 1976; Wolczanski, Threlkel & Santarsiero, 1983).

We thank J. E. Bercaw and R. E. Marsh for helpful discussions, and the National Science Foundation for support through grants CHE-82-19039 and CHE-83-03735.

References

BRAUER, D. J. & KRUGER, C. (1972). *Organomet. Chem.* **42**, 129.

BROWN, C. J. (1966). *Acta Cryst.* **21**, 153–158.

CHANG, C. H., PORTER, R. E. & BAUER, S. H. (1970). *J. Am. Chem. Soc.* **92**, 5313–5318.

DUCHAMP, D. J. (1964). *CRYM* Computing System. California Institute of Technology, USA.

DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules.* Ithaca, NY: Cornell Univ. Press.

FACHINETTI, G., FLORIANI, C., MARCHETTI, F. & MERLINO, S. (1976). *J. Chem. Soc. Chem. Commun.* p. 522.

GAMBROTTA, S., BASSOBERT, M., FLORIANI, C. & GUASTINI, C. (1982). *J. Chem. Soc. Chem. Commun.* pp. 374–375.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MOORE, E. J. (1984). PhD thesis, California Institute of Technology, Pasadena, CA, USA.

MOORE, E. J., STRAUS, D. A., ARMANTROUT, J., SANTARSIERO, B. D., GRUBBS, R. H. & BERCAW, J. E. (1983). *J. Am. Chem. Soc.* **105**, 2068–2070.

TROMBETTI, A. (1978). *Can. J. Phys.* **46**, 1005–1011.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

WOLCZANSKI, P. T., THRELKEL, R. S. & SANTARSIERO, B. D. (1983). *Acta Cryst.* C**39**, 1330–1333.

Acta Cryst. (1988). C**44**, 435–437

Structure of Potassium Triaqua(ethylenediaminetetraacetato)neodymate(III) Pentahydrate

BY DUBRAVKA MATKOVIĆ-ČALOGOVIĆ

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, POB 153, 41000 Zagreb, Yugoslavia

(*Received 6 July* 1987; *accepted* 29 *October* 1987)

Abstract. $K[Nd(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$, $M_r = 615{\cdot}67$, orthorhombic, $Fdd2$, $a = 19{\cdot}944\,(9)$, $b = 36{\cdot}035\,(9)$, $c = 12{\cdot}276\,(8)$ Å, $V = 8823\,(7)$ Å^3, $Z = 16$, $D_x = 1{\cdot}854$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 26{\cdot}24$ cm^{-1}, $F(000) = 4944$, $T = 293$ K, $R = 0{\cdot}029$ for 3187 observed reflections. Distances from Nd to the coordinating atoms fit well in the pattern of decreasing distances in the series La^{3+}–Lu^{3+} as a result of lanthanide contraction: Nd—O(edta) 2·411 (4)–2·472 (2), Nd—O(water) 2·520 (4)–2·574 (4), Nd—N 2·709 (4) and 2·715 (4) Å.

Introduction. Crystal structures of several lanthanide edta complexes have been reported: $K[La(edta)(H_2O)_3].5H_2O$ (Hoard, Lee & Lind, 1965), $Na[Ln(edta)(H_2O)_3].5H_2O$, Ln = Tb (Lee, 1967), Dy (Nassimbeni, Wright, van Niekerk & McCallum, 1979), Pr, Gd, Sm (Templeton, Templeton, Zalkin & Ruben, 1982), Sm (Engel, Takusagawa & Koetzle, 1984), Ho (Templeton, Templeton & Zalkin, 1985), and $Cs[Yb(edta)(H_2O)_2].3H_2O$ (Nassimbeni, Wright, van Niekerk & McCallum, 1979). It was suggested that there should be a change from a nine-coordinated to an eight-coordinated complex in the lanthanide series La^{3+} to Lu^{3+} as a result of the decreasing ionic radii. Only the Yb complex has so far been found to be eight-coordinated. All nine-coordinated complexes have very similar structures and most of them crystallize in the orthorhombic space group $Fdd2$. Ho and Dy complexes have been found to crystallize in the monoclinic space group $Fd11$ which involves ordering of the occupancy of water molecule sites that were described as disordered or with high temperature factors in the other structures. The crystal structure of the title compound was determined to obtain more information on the Nd–ligand distances.

Experimental. Purple crystals of $K[Nd(edta)(H_2O)_3].5H_2O$ were obtained from an aqueous solution of $K_2Nd(OH)(edta).4H_2O$ (Djordjević & Vuletić, 1980) in an attempt to grow single crystals of the hydroxo complex. Single crystal (longest dimensions along the a, b and c crystallographic axes 0·37 × 0·62 × 0·55 mm) was used for X-ray analysis. Intensities were measured on a Philips PW 1100 diffractometer (Mo $K\alpha$ radiation, graphite monochromator) in the range $4 < 2\theta < 60°$ ($0 \leq h \leq 28$, $0 \leq k \leq 50$, $0 \leq l \leq 17$). Unit-cell parameters were determined by least-squares refinement of 16 reflections, $12 < 2\theta < 16°$. Intensity data were collected in the $\theta/2\theta$ mode, scan speed 0·04° s^{-1}, scan width 1·2°. The intensity variation of standard reflections (391, 0,12,0, 602) measured every 2 h showed

0108-2701/88/030435-03$03.00