

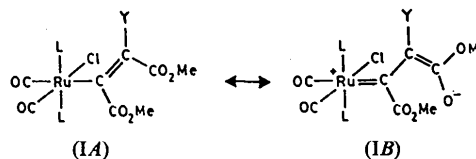
[Ru(CO)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)(C<sub>6</sub>H<sub>4</sub>)}(PMe<sub>2</sub>Ph)<sub>2</sub>] [1.914 (5) Å] (Crook *et al.*, 1990) and [Ru(CO)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)Cl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>] [1.91 (2) Å] (Holland, Howard & Mawby, 1983). For the latter complex, this increased length of the Ru—CO bond is reflected in the lability of the carbonyl ligand towards substitution.

The Ru—P bond lengths are equal to within expected error [2.385 (2) and 2.383 (2) Å] but are significantly longer than those in [Ru(CO)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)(C<sub>6</sub>H<sub>4</sub>)}(PMe<sub>2</sub>Ph)<sub>2</sub>] [2.362 (1) and 2.364 (1) Å] (Crook *et al.*, 1990).

The packing in the crystal is largely stabilized by van der Waals forces. There are five intermolecular contacts of less than 3.5 Å between non-H atoms. Four of these are with the molecule which is related by the symmetry operations 0.5 + x, 0.5 - y, -z. The contacts are: O(2)⋯C(1) 3.291; O(2)⋯C(4) 3.368; O(3)⋯C(28) 3.406; O(3)⋯C(20) 3.203 Å. The other contact is with the molecule symmetry-related by 0.5 - x, -y, 0.5 + z, and is C(25)⋯C(4) 3.475 Å. The closest contact between H atoms is H(301)⋯H(302) (2.262 Å) to the molecule related by 0.5 + x, 0.5 - y, -z.

There remains the question as to how the complexes (IV) are formed. It is clear from the NMR spectra of the vinyl complexes [Ru(CO)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)(C<sub>6</sub>H<sub>4</sub>X-4)}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>] that they are produced from [Ru(CO)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>X-4)Cl(PMe<sub>2</sub>Ph)<sub>2</sub>] and MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me in a single isomeric form, but it is also evident that *one* of their decomposition pathways [either to (II) or to (IV)] must involve a rearrangement of the vinyl ligand. One possibility is that, under the conditions used for

the thermal decompositions, rotation can occur about the C=C double bond of the vinyl ligand. This bond is unexpectedly long [1.41 (3) Å] in the related complex [Ru(CO)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)Cl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>], suggesting that resonance structure (1B), where L = PMe<sub>2</sub>Ph and Y = Cl or C<sub>6</sub>H<sub>4</sub>X-4, may make a significant contribution to the bonding in these vinyl complexes, reducing the bond order and the barrier to rotation about the C=C bond.



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#### References

- CROOK, J. R., CHAMBERLAIN, B. & MAWBY, R. J. (1989). *J. Chem. Soc. Dalton Trans.* pp. 465–470.  
 CROOK, J. R., GIORDANO, F., MAWBY, R. J., REID, A. J. & REYNOLDS, C. D. (1990). *Acta Cryst.* **C46**, 41–44.  
 HOLLAND, P. R., HOWARD, B. & MAWBY, R. J. (1983). *J. Chem. Soc. Dalton Trans.* pp. 231–237.  
 KOMIYA, S., ITO, T., COWIE, M., YAMAMOTO, A. & IBERS, J. A. (1976). *J. Am. Chem. Soc.* **98**, 3874–3884.  
 MALLINSON, M. D. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 RAGHAVAN, N. V. & DAVIES, R. E. (1975). *J. Cryst. Mol. Struct.* **5**, 163–176.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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## Structure of Bis(4-aminobenzenesulfonato-*O*)heptaaquaneodymium 4-Aminobenzenesulfonate Hydrate

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**Abstract.** [Nd(C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub>S)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>][C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub>S].H<sub>2</sub>O, *M<sub>r</sub>* = 804.9, orthorhombic, *Pcab*, *a* = 32.017 (9), *b* = 23.557 (7), *c* = 7.933 (3) Å, *V* = 5983 (4) Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.78, *D<sub>x</sub>* = 1.787 (1) Mg m<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ = 15.3 mm<sup>-1</sup>, *F*(000) = 3256, *T* = 303 (1) K, final *R* = 0.054 for 3935 reflections. The Nd ions are surrounded by seven water molecules and two 4-aminobenzenesulfonate anions.

**Introduction.** This work reports the structure of neodymium 4-aminobenzenesulfonate. Our interest in this complex ensues from our general interest in lanthanide complexes with N-donor ligands.

**Experimental.** The title compound was prepared by adding freshly precipitated neodymium hydroxide to a hot aqueous solution of 4-aminobenzenesulfonic

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$U_{eq}$
Nd	0.13940 (2)	0.05139 (2)	0.19834 (7)	0.0176 (1)
S1	0.19166 (7)	-0.0344 (1)	0.5548 (3)	0.0204 (7)
S2	0.16462 (9)	0.1597 (1)	0.5242 (3)	0.0281 (8)
S3	0.5200 (1)	0.5992 (1)	0.5327 (5)	0.042 (1)
O11	0.1741 (3)	-0.0065 (3)	0.4091 (9)	0.038 (3)
O21	0.1622 (2)	-0.0365 (3)	0.6920 (9)	0.035 (3)
O31	0.2321 (2)	-0.0109 (3)	0.6081 (11)	0.045 (3)
O12	0.1452 (2)	0.1355 (3)	0.3711 (10)	0.036 (3)
O22	0.2093 (3)	0.1677 (4)	0.4951 (13)	0.059 (4)
O32	0.1546 (3)	0.1277 (4)	0.6715 (11)	0.065 (4)
O13	0.4834 (4)	0.5990 (5)	0.4333 (15)	0.104 (6)
O23	0.5063 (3)	0.5777 (4)	0.6947 (15)	0.078 (5)
O33	0.5569 (3)	0.5701 (4)	0.4838 (14)	0.074 (4)
OW1	0.0992 (2)	-0.0387 (3)	0.1838 (9)	0.035 (3)
OW2	0.2186 (2)	0.0828 (3)	0.2279 (10)	0.039 (3)
OW3	0.1114 (2)	0.0370 (3)	-0.0945 (9)	0.031 (2)
OW4	0.0720 (2)	0.1012 (3)	0.1597 (9)	0.033 (3)
OW5	0.0923 (2)	0.0396 (3)	0.4559 (9)	0.035 (3)
OW6	0.1856 (2)	-0.0115 (4)	0.0313 (10)	0.045 (3)
OW7	0.1566 (2)	0.1330 (3)	0.0189 (10)	0.037 (3)
OW8	-0.0259 (3)	0.4754 (5)	0.3648 (13)	0.078 (5)
N1	0.2127 (3)	-0.2276 (3)	0.3726 (11)	0.027 (3)
N2	0.0918 (3)	0.3902 (4)	0.6015 (14)	0.045 (4)
N3	0.5634 (3)	0.8404 (4)	0.6533 (13)	0.039 (3)
C11	0.2006 (3)	-0.1055 (4)	0.4920 (12)	0.020 (3)
C21	0.1747 (3)	-0.1302 (4)	0.3730 (14)	0.024 (3)
C31	0.1793 (3)	-0.1868 (5)	0.3347 (14)	0.029 (4)
C41	0.2093 (3)	-0.2189 (4)	0.4136 (13)	0.024 (3)
C51	0.2351 (3)	-0.1941 (5)	0.5273 (15)	0.029 (4)
C61	0.2305 (3)	-0.1381 (4)	0.5676 (14)	0.024 (3)
C12	0.1433 (3)	0.2275 (5)	0.5417 (13)	0.026 (3)
C22	0.1639 (4)	0.2689 (5)	0.6325 (16)	0.035 (4)
C32	0.1479 (4)	0.3222 (5)	0.6474 (18)	0.044 (5)
C42	0.1086 (4)	0.3344 (5)	0.5830 (14)	0.031 (4)
C52	0.0876 (4)	0.2935 (5)	0.4938 (16)	0.038 (4)
C62	0.1037 (4)	0.2402 (5)	0.4704 (15)	0.035 (4)
C13	0.5331 (3)	0.6693 (4)	0.5656 (13)	0.026 (3)
C23	0.5700 (4)	0.6929 (5)	0.5017 (15)	0.031 (4)
C33	0.5795 (4)	0.7484 (5)	0.5279 (15)	0.035 (4)
C43	0.5540 (3)	0.7826 (4)	0.6267 (14)	0.028 (3)
C53	0.5176 (3)	0.7603 (5)	0.6937 (14)	0.030 (3)
C63	0.5072 (4)	0.7038 (5)	0.6610 (14)	0.031 (4)

acid. After a few days water-soluble violet-brown needles were formed. A specimen  $0.4 \times 0.1 \times 0.02$  mm was cut from a larger crystal.  $D_m$  was measured by flotation in  $C_2H_4Br_2/CHCl_3$ . Oscillation and Weissenberg photographs allowed the space group to be established. A KM4 diffractometer with  $\kappa$  geometry and Cu  $K\alpha$  radiation was used for data collection, variable  $\omega/2\theta$  scan,  $4 < 2\theta < 130^\circ$ . Lattice parameters were determined using 25 reflections with  $40 < 2\theta < 50^\circ$ . Three standards measured every 50 reflections showed mean relative e.s.d. of 2.1%. 5874 intensities were measured, 4317 with  $I \geq 2\sigma(I)$ , of which 3935 were unique;  $R_{int} = 0.021$ ; index range  $h 0 \rightarrow 37$ ,  $k 0 \rightarrow 27$ ,  $l 0 \rightarrow 9$ . Absorption corrections, applied using the locally modified program *ABSORB* (Ugozzoli, 1987), were between 0.77 and 1.47. The structure was solved with *SHELXS86* (Sheldrick, 1986) and refined with locally modified *SHELX76* (Sheldrick, 1976). Neutral-atom scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV); real and imaginary components of anomalous dispersion were included for all non-H atoms. The Nd atoms were located

Table 2. Distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the Nd coordination sphere

Nd—O11	2.427 (8)	Nd—O12	2.416 (7)
Nd—OW1	2.485 (7)	Nd—OW2	2.652 (7)
Nd—OW3	2.513 (7)	Nd—OW4	2.475 (7)
Nd—OW5	2.555 (7)	Nd—OW6	2.478 (8)
Nd—OW7	2.455 (7)		
O12—Nd—O11	92.0 (3)		
OW1—Nd—O11	77.8 (3)	OW1—Nd—O12	140.0 (3)
OW2—Nd—O11	70.0 (3)	OW2—Nd—O12	69.4 (3)
OW2—Nd—OW1	137.5 (3)		
OW3—Nd—O11	136.4 (3)	OW3—Nd—O12	131.5 (3)
OW3—Nd—OW1	70.0 (3)	OW3—Nd—OW2	117.4 (3)
OW4—Nd—O11	138.7 (3)	OW4—Nd—O12	75.4 (3)
OW4—Nd—OW1	87.0 (3)	OW4—Nd—OW2	135.4 (3)
OW4—Nd—OW3	68.8 (3)		
OW5—Nd—O11	70.0 (3)	OW5—Nd—O12	71.4 (3)
OW5—Nd—OW1	68.8 (3)	OW5—Nd—OW2	121.6 (3)
OW5—Nd—OW3	120.9 (3)	OW5—Nd—OW4	68.7 (3)
OW6—Nd—O11	76.1 (3)	OW6—Nd—O12	138.4 (3)
OW6—Nd—OW1	76.9 (3)	OW6—Nd—OW2	69.1 (3)
OW6—Nd—OW3	68.8 (3)	OW6—Nd—OW4	137.5 (3)
OW6—Nd—OW5	135.7 (3)		
OW7—Nd—O11	137.5 (3)	OW7—Nd—O12	70.7 (3)
OW7—Nd—OW1	139.3 (3)	OW7—Nd—OW2	67.6 (3)
OW7—Nd—OW3	69.5 (3)	OW7—Nd—OW4	75.7 (3)
OW7—Nd—OW5	133.0 (3)	OW7—Nd—OW6	91.4 (3)

from a Patterson map and the remaining non-H atoms from subsequent difference syntheses; C-bonded H atoms were placed geometrically and water H atoms were located from difference syntheses or placed on the basis of hydrogen-bond geometry. Final full-matrix least-squares refinement based on  $F$  [non-H atoms anisotropic; C-bonded H atoms isotropic and constrained with C—H = 0.91 (3)  $\text{\AA}$  and common temperature factor  $U = 0.020$  (7)  $\text{\AA}^2$ ; O- and N-bonded H atoms geometrically fixed with common temperature factor  $U = 0.15$  (2)  $\text{\AA}^2$ ] converged at  $R = 0.054$ ,  $wR = 0.050$  [ $w = 1/\sigma^2(F)$ ], maximum shift/e.s.d. = 0.15,  $\Delta\rho$  between -0.14 and 0.17  $e \text{\AA}^{-3}$  (highest peaks around Nd atoms), for 418 parameters.

**Discussion.** Final atomic parameters are given in Table 1;\* the geometry of the coordination environment of the Nd ions is shown in Table 2. The structure consists of the complex cation [of which an *ORTEP* view (Johnson, 1976) is given in Fig. 1], a non-coordinated 4-aminobenzenesulfonate anion and a water of hydration. The overall coordination pattern (two coordinated sulfonate anions plus one uncoordinated) resembles those reported for lanthanide 2-naphthalenesulfonates (Ohki, Suzuki, Nakamura, Shimoi & Ouchi, 1985) and *p*-toluenesulfonates (Ohki, Suzuki, Takeuchi & Ouchi, 1988). The

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bond interactions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55034 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0260]

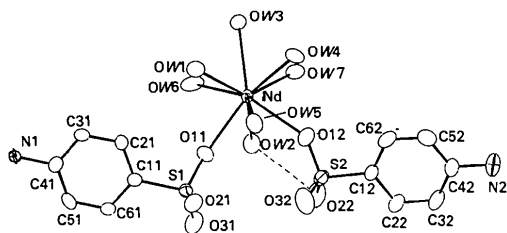


Fig. 1. The complex cation. The intramolecular hydrogen bond is marked with the dashed line. The numbering scheme of the third anion follows those of the two anions shown.

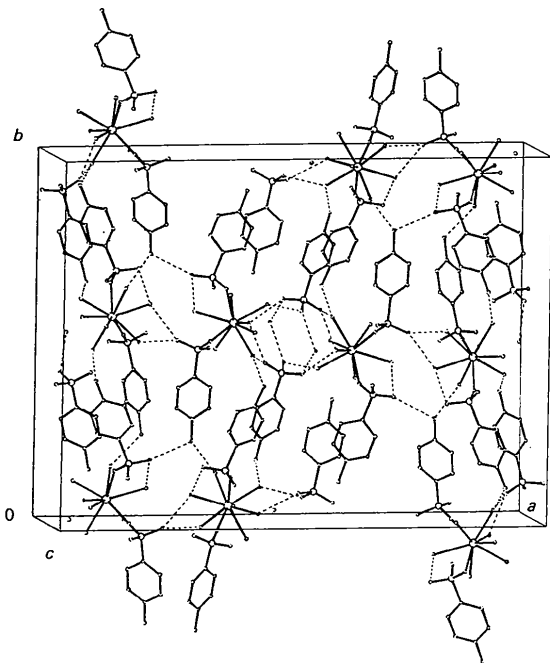


Fig. 2. View of the crystal structure. The dashed lines represent the hydrogen bonds.

difference is in the lanthanide coordination number: eight for the quoted structures, and nine for the present one. All bond distances lie within observed ranges. The coordination polyhedron of Nd1 may best be described as a tricapped trigonal prism in which upper and lower bases are defined by O11, OW6, OW1 and O12, OW7, OW4 respectively, OW2, OW3 and OW4 being the caps;  $\Delta = 0.0063 \text{ \AA}^2$  [ $\Delta = \sum d_i^2/9$ , where  $d_i$  is the distance between the real position of the  $i$ th atom and the relevant vertex in the ideal least-squares-fitted polyhedron (Drew, 1977)]. The two best capped square antiprisms found may be described as: (i) non-capped base O12, OW2, O11, OW5; capped base OW7, OW6, OW1, OW4; cap OW3;  $\Delta = 0.0644 \text{ \AA}^2$ ; and (ii) non-capped base OW2, OW7, OW3, OW6; capped base O12, OW4, OW1, O11; cap OW5;  $\Delta = 0.0522 \text{ \AA}^2$ . The structure is held together by an elaborate network of intermolecular hydrogen bonds. The crystal packing is shown in Fig. 2.

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#### References

- DREW, M. G. B. (1977). *Coord. Chem. Rev.* **24**, 179–275.  
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 OHKI, Y., SUZUKI, Y., NAKAMURA, M., SHIMOI, M. & OUCHI, A. (1985). *Bull. Chem. Soc. Jpn.* **58**, 2968–2974.  
 OHKI, Y., SUZUKI, Y., TAKEUCHI, T. & OUCHI, A. (1988). *Bull. Chem. Soc. Jpn.* **61**, 393–405.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 UGOZZOLI, F. (1987). *Comput. Chem.* **11**, 109–120.

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## A Permethylcyclopentadienyl Carbollide Scandium Complex, $\text{Sc}_2\text{Si}_4\text{O}_3\text{C}_{50}\text{B}_{18}\text{Li}_2\text{H}_{114}$

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**Abstract.** Tris(tetrahydrofuran)lithium lithium bis[3-bis(trimethylsilyl)methyl-3-( $\eta^5$ -pentamethylcyclopent-

tadienyl)-1,2-dicarba-3-scanda-*closo*-dodecaborate-(1-)],  $[\text{Li}(\text{C}_4\text{H}_8\text{O})_3] \cdot \text{Li}[\text{Sc}(\text{C}_2\text{B}_9\text{H}_{11})(\text{C}_{10}\text{H}_{15})\text{CH}\{\text{Si}(\text{CH}_3)_3\}_2]_2$ ,  $M_r = 1174.16$ , triclinic,  $P\bar{1}$ ,  $a = 8.924(4)$ ,  $b = 18.467(5)$ ,  $c = 22.165(3) \text{ \AA}$ ,  $\alpha = 91.42(2)$ ,  $\beta =$

\* Contribution No. 8430.