

and four H<sub>2</sub>O molecules. The Ag atom occupies the crystallographic centre of symmetry and also the twofold axis (Fig. 1). One nitrate is located on a twofold axis. In the cation, the Ag atom and the two Co atoms are bridged by two pyrazines. Two O atoms from water molecules also coordinate to the Ag atom. The angles of both N—Ag—N and O—Ag—O are 180.0°. The Ag—O bond distance of 2.585 Å, which is generally considered as a weak bond, is longer than that of Ag—N 2.302 Å, and forms the square-planar coordination. The Co atom is coordinated by six N atoms, five from NH<sub>3</sub> groups and one from pyrazine, forming an octahedral coordination, with the two pyrazine rings being in the same plane. The pyrazine plane is about 86° out of the plane Co—N(3)—N(4)—N(5)—N(6) and 102° out of the plane Ag—N(1)—N(1)—O—O'. The C—C and C—N bond distances of the bridging pyrazines are not significantly different from pyrazine itself (C—N 1.334 Å, C—C 1.378 Å). The distance between the cation and anion is about 3.4–4.0 Å, showing the existence of strong Coulombic forces. Some non-bonded distances for O—O and N—O are less than 3 Å, indicating that there are hydrogen bonds.

The structure of the pyrazine-bridged heterobinuclear complex (II) consists of one [(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)Cu(μ-C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)Co(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup> cation and five ClO<sub>4</sub><sup>-</sup> anions. The pyrazine group bridges the Cu and Co atoms (Fig. 2). The Cu atom shows a distorted square-planar coordination, surrounded by four approximately planar N atoms, N(7) from pyrazine and N(8), N(9) and N(10) from diethylenetriamine. As in Cu,Zn—SOD (superoxide dismutase) (Tainer, Getzoff, Beem, Richardson & Richardson, 1982), the bond length off Cu—N is about 2.0 Å, but there is

no Cu—O bond at the axial position, and the angles of N—Cu—N are different. In Cu,Zn—SOD, N(1)—Cu—N(3) = 160 and N(2)—Cu—N(4) = 130°, and in the cation of complex (II), N(1)—Cu—N(3) = 169.2 and N(2)—Cu—N(4) = 176.8°. The Co atom is coordinated by six N atoms, five from NH<sub>3</sub> groups and one from pyrazine, forming an octahedral coordination. The bond distances and angles around the Co atom are in accord with the corresponding values in the literature (Davis, Dewan & Lippard, 1981).

The pyrazine group shows a good planar conformation. It makes an angle of about 70° with the plane of diethylenetriamine and thus reduces the repulsion force of two planes, forming a stable conformation.

Each ClO<sub>4</sub><sup>-</sup> anion forms a tetrahedron as usual. The average bond distance of Cl—O is 1.415 Å and O—Cl—O bond angles range from 98.0 to 117.0°. The distance between cations and anions is about 5 Å showing the existence of strong Coulombic forces. Some distances of N...O are less than 3.2 Å, which implies that there are either hydrogen bonds or close contacts.

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## Structure of 1,2,3-Tris(dimethylamino)cyclopropenylium Aquatetrachlorooxoniobate(V)

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**Abstract.** [C<sub>9</sub>H<sub>18</sub>N<sub>3</sub>][NbCl<sub>4</sub>O(H<sub>2</sub>O)], *M<sub>r</sub>* = 436.997, triclinic, *P*1, *a* = 12.2716 (9), *b* = 8.9682 (5), *c* = 8.7625 (5) Å, *α* = 70.203 (9), *β* = 88.242 (5), *γ* = 71.299 (5)°, *V* = 856.137 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.695 g cm<sup>-3</sup>, Mo *Kα*, *λ* = 0.70926 Å, *μ* = 13.042 cm<sup>-1</sup>, *F*(000) = 440, room temperature, final

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Table 1. Fractional coordinates and  $U_{\text{eq}}/U_{\text{iso}}$  values ( $\text{\AA}^2$ )

No. in Figures	Occupation	x	y	z	U
1	Nb(01)	1.000	0.000	0.000	0.0381
2	O(11)	1.000	0.1152 (4)	-0.1722 (6)	0.0114 (7)
3	Cl(12)	1.000	-0.1432 (2)	-0.1292 (3)	0.0574 (2)
4	Cl(13)	1.000	-0.0572 (2)	0.0938 (3)	-0.2826 (2)
5	Cl(14)	1.000	0.1050 (2)	0.1939 (3)	-0.0594 (3)
6	Cl(15)	1.000	0.0136 (2)	-0.0225 (3)	0.2780 (2)
7	O(10)	1.000	-0.1529 (4)	0.2501 (7)	-0.0222 (7)
10	Nb(02)	1.000	0.50995 (5)	0.55386 (7)	0.07325 (7)
11	O(21)	1.000	0.6299 (4)	0.3915 (6)	0.0739 (5)
12	Cl(22)	1.000	0.3743 (2)	0.4080 (2)	0.1394 (2)
13	Cl(23)	1.000	0.4458 (2)	0.6430 (3)	-0.2073 (2)
14	Cl(24)	1.000	0.5904 (2)	0.7727 (3)	0.0048 (3)
15	Cl(25)	1.000	0.5323 (2)	0.5233 (3)	0.3521 (2)
16	O(20)	1.000	0.3414 (4)	0.7800 (7)	0.0710 (6)
19	C(10)	1.000	0.0457 (6)	0.5433 (8)	0.5547 (7)
20	N(11)	1.000	0.1405 (5)	0.5671 (7)	0.5913 (7)
21	C(12)	1.000	0.2353 (7)	0.555 (1)	0.482 (1)
25	C(13)	1.000	0.144 (1)	0.640 (2)	0.713 (2)
29	C(20)	1.000	-0.0633 (3)	0.5446 (9)	0.5864 (8)
30	N(21)	1.000	-0.1523 (5)	0.5689 (8)	0.6800 (8)
31	C(22)	1.000	-0.150 (1)	0.652 (2)	0.790 (2)
35	C(23)	1.000	-0.2664 (7)	0.583 (1)	0.620 (1)
39	C(30)	1.000	-0.0163 (6)	0.5006 (8)	0.4582 (8)
40	N(31)	1.000	-0.0236 (5)	0.4462 (7)	0.3402 (7)
41	C(32)	1.000	-0.130 (1)	0.434 (2)	0.292 (1)
45	C(33)	1.000	0.0684 (9)	0.429 (1)	0.232 (1)
49	C(40)	1.000	0.5291 (6)	0.0713 (8)	0.4962 (8)
50	N(41)	1.000	0.6199 (5)	0.0332 (8)	0.4100 (8)
51	C(41)	1.000	0.605 (1)	-0.008 (1)	0.270 (1)
55	C(43)	1.000	0.7240 (8)	0.067 (2)	0.435 (1)
59	C(50)	1.000	0.4803 (6)	0.1240 (8)	0.6164 (7)
60	N(51)	1.000	0.4857 (5)	0.1841 (7)	0.7323 (6)
61	C(52)	1.000	0.593 (1)	0.205 (1)	0.772 (2)
65	C(53)	1.000	0.3914 (9)	0.202 (1)	0.836 (1)
69	C(60)	1.000	0.4190 (5)	0.0761 (7)	0.5265 (7)
70	N(61)	1.000	0.3226 (5)	0.0557 (8)	0.4845 (7)
71	C(62)	1.000	0.2271 (7)	0.070 (1)	0.592 (1)
75	C(63)	1.000	0.3232 (9)	-0.019 (1)	0.368 (1)

$R = 0.0344$  for  $F$  and 2141 reflections. The crystal structure consists of chains of  $[\text{NbOCl}_4(\text{OH}_2)]^-$  square bipyramids along the  $[110]$  direction connected by trigonal planar  $[\text{C}_3\{\text{N}(\text{CH}_3)_2\}_3]^+$  ions.

**Introduction.** The structure of the tris(dimethylamino)cyclopropenylum ion is reported by Ku & Sundaralingam (1972). Our structure determination was started as part of investigations of the salts of the tris(dimethylamino)cyclopropenylum ion and inorganic complex anions (Yoshida & Tawara, 1971; Weiss & Schloter, 1975).

In several cases these salts show – like the title compound – interesting outer-sphere-charge-transfer interactions between cation and anion leading to intensely coloured solids, although the ionic components of the salts are colourless (Weiss, 1979).

**Experimental.** A solution of 1.019 g tris(dimethylamino)cyclopropenylum chloride in 25 ml conc. hydrochloric acid was added to 1.352 g  $\text{NbCl}_5$  dissolved in 100 ml hydrochloric acid. After stirring for 2 h the resulting mixture was filtered. Cooling the filtrate to 263 K led to orange crystals of the title compound. The specimen used for the structure determination had dimensions  $0.30 \times 0.40 \times 0.50$  mm and was packed in a thin film of glue on

account of the hygroscopic properties of the title compound.

All measurements were performed on a PW 1100 instrument, that was rebuilt and equipped with additional facilities (Gomm, 1991). Details of measurement:  $\omega$ - $2\theta$  scan, modified Lehmann–Larsen profile analysis; lattice parameters derived from 45 reflections with  $15 \leq \theta \leq 18^\circ$ ; absorption correction using a modified version of the program *CAMEL JOCKEY* (Flack, 1975) based on empirical  $\psi$ -scan data, max. and min. correction factor 1.45 and 2.10; intensities collected for  $-12 \leq h \leq 12$ ,  $-9 \leq k \leq 9$ ,  $-9 \leq l \leq 9$ ,  $\theta_{\text{max}} = 22^\circ$ . Four standard reflections, no significant variation, 4282 reflections measured, 2141 unique reflections, no unobserved reflections omitted;  $R_{\text{int}}$  based on  $F$  is 0.0264.

The Nb and Cl atoms were determined using the Patterson method. From a Fourier map the rest of the non-H atoms were derived. A subsequent difference Fourier map revealed all H atoms. Full-matrix least squares based on  $F$ ; weights derived from experimental standard deviations,  $w = 1/\sigma(F)$ . In the final stage anisotropic temperature parameters were used for all non-H atoms and a common isotropic temperature parameter for the H atoms; the results are given in Table 1.\* The final  $R$  values are:  $R = 0.034$ ,  $wR = 0.039$ ,  $S = 2.37$ , maximum shift to e.s.d. ratio 0.01.

Effects of anomalous dispersion are within the range of the e.s.d. of the measurement. Maximum and minimum electron density residuals are  $\rho_{\text{max}} = 0.85$ ,  $\rho_{\text{min}} = 0.71 \text{ e \AA}^{-3}$ , respectively. Extinction corrections were applied according to the Zachariasen (1968) formula; maximum extinction factor was 2.021; form factor tables from *International Tables for X-ray Crystallography* (1962, Vol. III, pp. 260–270). All computations were performed on a MicroVAX II computer using an adapted version of the program system *ATARI CRYSTAN88* (1989).

**Discussion.** Distances and angles are given in Table 2.

The distances and angles of the cation are in good agreement with those found in  $[\text{C}_3\{\text{N}(\text{CH}_3)_2\}_3]^+ \cdot \text{ClO}_4^-$  by Ku & Sundaralingam (1972). The anion  $[\text{NbOCl}_4(\text{OH}_2)]^-$  consists of a square pyramidal  $\text{NbOCl}_4^-$  ion to which an  $\text{H}_2\text{O}$  molecule is attached in a *trans* position to the O atom. There are some examples of  $\text{NbOCl}_4^-$  ions coordinated by solvent molecules (Cotton, Diebold

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53942 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (Å) and angles (°)

C(10)—N(11)	1.316 (5)	C(43)—N(41)	1.444 (7)
C(10)—C(20)	1.358 (5)	C(50)—N(51)	1.313 (5)
C(10)—C(30)	1.373 (6)	C(50)—C(40)	1.345 (5)
N(11)—C(10)	1.316 (5)	C(50)—C(60)	1.358 (6)
N(11)—C(13)	1.433 (9)	N(51)—C(50)	1.313 (5)
N(11)—C(12)	1.485 (6)	N(51)—C(53)	1.453 (6)
C(12)—N(11)	1.485 (6)	N(51)—C(52)	1.460 (8)
C(13)—N(11)	1.433 (9)	C(52)—N(51)	1.460 (8)
C(20)—N(21)	1.352 (5)	C(53)—N(51)	1.453 (6)
C(20)—C(10)	1.358 (5)	C(60)—N(61)	1.333 (5)
C(20)—C(30)	1.360 (5)	C(60)—C(50)	1.358 (6)
N(21)—C(20)	1.352 (5)	C(60)—C(40)	1.359 (5)
N(21)—C(22)	1.412 (9)	N(61)—C(60)	1.333 (5)
N(21)—C(23)	1.461 (6)	N(61)—C(63)	1.398 (8)
C(22)—N(21)	1.412 (9)	N(61)—C(62)	1.479 (5)
C(23)—N(21)	1.461 (6)	C(62)—N(61)	1.479 (5)
C(30)—N(31)	1.301 (5)	C(63)—N(61)	1.398 (8)
C(30)—C(20)	1.360 (5)	Nb(01)—O(11)	1.702 (2)
C(30)—C(10)	1.373 (6)	Nb(01)—Cl(12)	2.354 (2)
N(31)—C(30)	1.301 (5)	Nb(01)—O(10)	2.370 (2)
N(31)—C(32)	1.435 (8)	Nb(01)—Cl(13)	2.377 (1)
N(31)—C(33)	1.455 (6)	Nb(01)—Cl(15)	2.382 (1)
C(32)—N(31)	1.435 (8)	Nb(01)—Cl(14)	2.396 (2)
C(33)—N(31)	1.455 (6)	O(10)—Nb(01)	2.370 (2)
C(40)—N(41)	1.345 (5)	Nb(02)—O(21)	1.705 (2)
C(40)—C(50)	1.345 (9)	Nb(02)—Cl(24)	2.365 (2)
C(40)—C(60)	1.359 (5)	Nb(02)—Cl(22)	2.376 (2)
N(41)—C(40)	1.345 (5)	Nb(02)—Cl(25)	2.379 (1)
N(41)—C(42)	1.430 (7)	Nb(02)—O(20)	2.382 (2)
N(41)—C(43)	1.444 (7)	Nb(02)—Cl(23)	2.385 (1)
C(42)—N(41)	1.430 (7)	O(22)—Nb(02)	2.382 (2)
C(20)—C(10)—N(11)	149.7 (6)	C(63)—N(61)—C(60)	119.9 (2)
C(30)—C(10)—N(11)	150.6 (6)	C(62)—N(61)—C(60)	118.6 (2)
C(30)—C(10)—C(20)	59.7 (2)	C(62)—N(61)—C(63)	119.5 (2)
C(13)—N(11)—C(10)	120.8 (3)	Cl(12)—Nb(01)—O(11)	98.40 (1)
C(12)—N(11)—C(10)	119.4 (2)	O(10)—Nb(01)—O(11)	176 (2)
C(12)—N(11)—C(13)	118.4 (2)	O(10)—Nb(01)—Cl(12)	85.132 (9)
C(10)—C(20)—N(21)	148.6 (5)	Cl(13)—Nb(01)—O(11)	98.46 (2)
C(30)—C(20)—N(21)	150.7 (5)	Cl(13)—Nb(01)—Cl(12)	89.601 (7)
C(30)—C(20)—C(10)	60.7 (2)	Cl(13)—Nb(01)—O(10)	80.97 (2)
C(22)—N(21)—C(20)	118.2 (2)	Cl(15)—Nb(01)—O(11)	97.92 (1)
C(23)—N(21)—C(20)	119.0 (2)	Cl(15)—Nb(01)—Cl(12)	88.996 (6)
C(23)—N(21)—C(22)	116.4 (2)	Cl(15)—Nb(01)—O(10)	82.62 (1)
C(20)—C(30)—N(31)	149.3 (5)	Cl(15)—Nb(01)—Cl(13)	163.6 (1)
C(10)—C(30)—N(31)	150.9 (6)	Cl(14)—Nb(01)—O(11)	96.38 (1)
C(10)—C(30)—C(20)	59.6 (2)	Cl(14)—N(01)—Cl(12)	165.2 (2)
C(32)—N(31)—C(30)	121.2 (2)	Cl(14)—Nb(01)—O(10)	80.10 (1)
C(33)—N(31)—C(30)	120.4 (2)	Cl(14)—Nb(01)—Cl(13)	88.904 (8)
C(33)—N(31)—C(32)	117.3 (2)	Cl(14)—Nb(01)—Cl(15)	88.297 (7)
C(50)—C(40)—N(41)	151.1 (6)	Cl(24)—Nb(02)—O(21)	99.55 (1)
C(60)—C(40)—N(41)	148.6 (5)	Cl(22)—Nb(02)—O(21)	99.18 (1)
C(60)—C(40)—C(50)	60.3 (2)	Cl(22)—Nb(02)—Cl(24)	161.3 (2)
Cl(42)—N(41)—C(40)	119.2 (2)	Cl(25)—Nb(02)—O(21)	97.58 (1)
Cl(43)—N(41)—C(40)	120.8 (2)	Cl(25)—Nb(02)—Cl(24)	88.978 (8)
Cl(43)—N(41)—C(42)	118.6 (2)	Cl(25)—Nb(02)—Cl(22)	89.035 (6)
C(40)—C(50)—N(51)	150.1 (6)	O(20)—Nb(02)—O(21)	180 (3)
C(60)—C(50)—N(51)	149.6 (6)	O(20)—Nb(02)—Cl(24)	80.77 (1)
C(60)—C(50)—C(40)	60.3 (2)	O(20)—Nb(02)—Cl(22)	80.50 (1)
C(53)—N(51)—C(50)	119.0 (2)	O(20)—Nb(02)—Cl(25)	82.76 (1)
C(52)—N(51)—C(50)	119.4 (2)	Cl(23)—Nb(02)—O(21)	96.93 (1)
C(52)—N(51)—C(53)	120.8 (2)	Cl(23)—Nb(02)—Cl(24)	88.291 (8)
C(50)—C(60)—N(61)	152.4 (6)	Cl(23)—Nb(02)—Cl(22)	88.983 (7)
C(40)—C(60)—N(61)	148.2 (5)	Cl(23)—Nb(02)—Cl(25)	165.5 (2)
C(40)—C(60)—C(50)	59.3 (2)	Cl(23)—Nb(02)—O(20)	82.72 (1)

Roth, 1988). In comparison with the Nb—O distance of 1.99 Å in (NH<sub>4</sub>)NbOBr<sub>4</sub> found by Hoerner, Hiller & Straehle (1988), where the Nb atoms are connected by symmetrical linear oxo bridges forming chains of polymeric [NbOBr<sub>4</sub>]<sub>n</sub> anions, this Nb—OH<sub>2</sub> distance is long.

In our compound we observe another type of anionic chain formed by hydrogen bonding. An H atom of one [NbOCl<sub>4</sub>(OH)<sub>2</sub>] ion is bonded to the O atom at the apex of the next anion (Fig. 1). The observed H...O distances of 1.92 and 2.17 Å are in good agreement with those values given in the literature. The hydrogen bonds connect neighbouring anions to form chains in the [110] direction.

A careful inspection of the neighbourhood of the H<sub>2</sub>O groups shows significant differences indicating a two-membered chain. The coordination polyhedron (Fig. 2a) of H<sub>2</sub>O(10) shows a relatively short distance (O10—N21 3.15 Å) to one CN(CH<sub>3</sub>)<sub>2</sub> group of a cation. This spatial relation is missing for H<sub>2</sub>O(20) (Fig. 2b) (O—N distances > 4.0 Å). Similar relations can be found in related compounds. A more detailed publication with respect to the connection patterns in this class of compounds is in preparation.

Compounds containing the [NbOCl<sub>4</sub>(OH)<sub>2</sub>]<sup>−</sup> ion such as the tetraethylammonium salt (Kanzelmeyer, Ryan & Freund, 1956) or the pyridinium salt (Weinland & Storz, 1907) are colourless solids. The salt [C<sub>3</sub>{N(CH<sub>3</sub>)<sub>2</sub>}<sub>3</sub>]<sup>+</sup>.ClO<sub>4</sub><sup>−</sup> (Ku & Sundaralingam, 1972) is colourless too. So the intense orange colour of the title compound can be attributed to an interionic outer-sphere-charge-transfer transition. This conclusion is supported by the observation that the colour vanishes in solution and by the value of the shortest

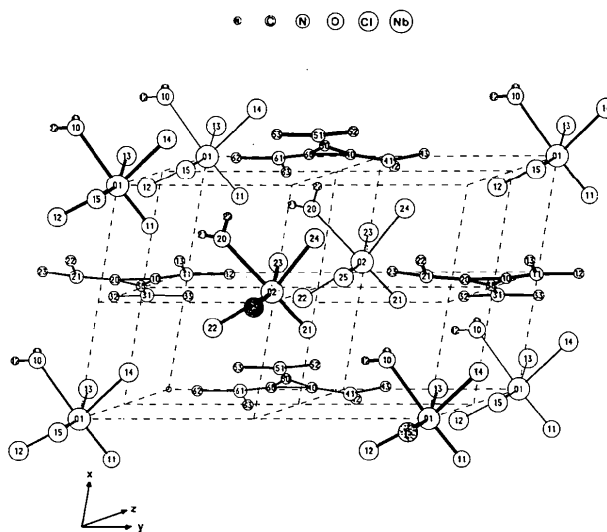


Fig. 1. The structure of the title compound.

& Roth, 1988) or other ions (Dewan, Kepert, Raston & White, 1975; Mueller & Lorenz, 1980) in the same way. In all these structures distances and angles within the NbOCl<sub>4</sub><sup>−</sup> ion reported are in agreement with our results. A salt containing an [NbOCl<sub>4</sub>(OH)<sub>2</sub>]<sup>−</sup> group is reported by Klingelhofer & Mueller (1984) with a rather long Nb—OH<sub>2</sub> distance of 2.49 Å, and the H-atom positions could not be determined. We found much shorter Nb—OH<sub>2</sub> distances of 2.37 and 2.38 Å, which are in good agreement with the Nb—O distance in the tetrahydrofuran adduct of NbOCl<sub>4</sub><sup>−</sup> (Cotton, Diebold &

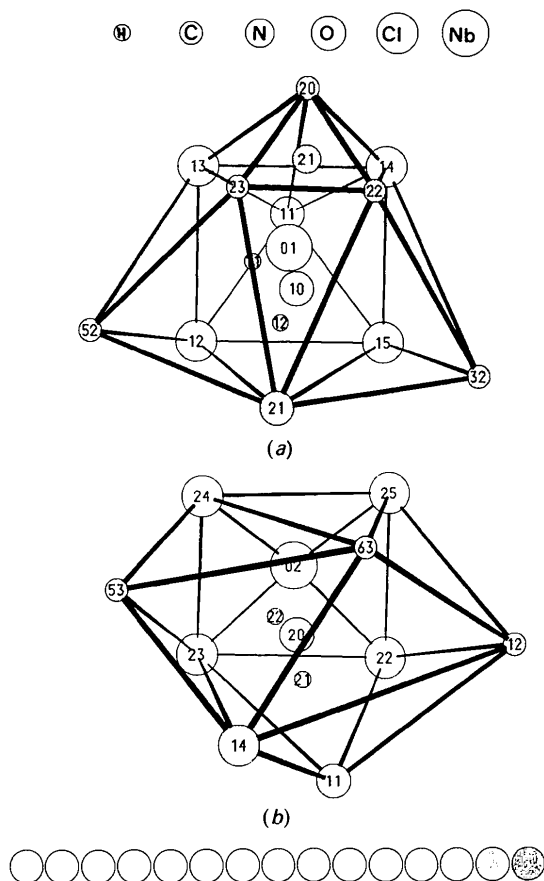


Fig. 2. The neighbourhood of the H<sub>2</sub>O groups; (a) H<sub>2</sub>O(10) and (b) H<sub>2</sub>O(20).

Cl—N distance of 3.49 Å, which is in the typical range for interionic charge-transfer salts. A detailed publication with respect to the theoretical approach to the effect is in preparation.

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## Long Zr—S Bonds in the Structure of the Stereochemically Nonrigid Complex, Bis( $\eta^5$ -cyclopentadienyl)(*N,N*-dimethyldithiocarbamato)phenoxyzirconium(IV)

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**Abstract.** C<sub>19</sub>H<sub>21</sub>NOS<sub>2</sub>Zr, *M<sub>r</sub>* = 434.73, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 8.126 (6), *b* = 8.692 (7), *c* = 26.626 (12) Å,  $\beta$  = 98.19 (5)°, *V* = 1861 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.53,

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*D<sub>x</sub>* = 1.55 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71073 Å,  $\mu$  = 8.0 cm<sup>-1</sup>, *F*(000) = 888, *T* = 295 K, *R* = 0.12 for 5313 unique data, 2082 of which were observed. The expected bent-metallocene geometry is observed. The Zr—S bonds to the bidentate dithiocarbamate ligand (2.656 and 2.789 Å) are unusually long, thus