Johnson Matthey is gratefully thanked for a loan of Pt salts.

References

Farrugia, L. J., Howard, J. A. K., Mitrprachachon, P., Stone, F. G. A. & Woodward, P. (1981). *J. Chem. Soc. Dalton Trans.* pp. 162–170.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.

Orpen, A. G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2509–2516.

Stuart, D. & Walker, N. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1988). C**44**, 1309–1311

Structure of a Binuclear [(1*R*,2*R*)-*N*,*N*′-Disalicylidene-1,2-cyclohexanediamine]titanium(IV) Complex

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(*Received* 8 *March* 1988; *accepted* 22 *March* 1988)

Abstract. Dichloro[7,7′-(cyclohexylenedinitrilo)di-*o*-cresolato]-μ-oxo-dititanium(IV)–acetone (1/2), $[Ti_2(C_{20}H_{20}N_2O_2)_2Cl_2O].2C_3H_6O$, $M_r = 939{\cdot}6$, monoclinic, $C2$, $a = 22{\cdot}189\,(6)$, $b = 9{\cdot}616\,(2)$, $c = 23{\cdot}452\,(6)$ Å, $\beta = 115{\cdot}21\,(2)^\circ$, $V = 4527\,(2)$ Å^3, $Z = 4$, $D_m(C_6H_6/CCl_4) = 1{\cdot}44\,(3)$, $D_x = 1{\cdot}38$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}511$ mm^{-1}, $F(000) = 1963{\cdot}7$, $T = 299\,(1)$ K, final $R = 0{\cdot}045$ for 2421 observed unique reflections. This compound is a binuclear complex and has a pseudo center of symmetry at the bridging O(0) atom except for the (*R*,*R*)-1,2-cyclohexanediamine (*R*,*R*-chxn) moieties in the Schiff base. The Ti—O(0)—Ti angle is 168·3 (3)° and Ti—O(0) distances are 1·798 (6) and 1·814 (6) Å. The Ti atoms are coordinated octahedrally by two N and three O atoms and a Cl$^-$ ion with O(0) and Cl$^-$ *trans*.

Experimental. An orange crystal of dimensions 0·2 × 0·2 × 0·6 mm, crystallized from acetone and dichloromethane solution, sealed in a capillary tube together with mother liquor. Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Laue group $2/m$; cell parameters refined by least squares for 20 2θ values ($20 < 2\theta < 24^\circ$); intensity measurement performed to $2\theta = 45^\circ$ (h $-23\rightarrow23$, k $-10\rightarrow0$, l $0\rightarrow25$), θ–2θ scan. Variation of five standard reflections, $0{\cdot}99 \le \sum(|F_o|/|F_o|_{\rm initial})/5 \le 1{\cdot}01$. 3340 reflections measured, 2494 reflections observed with $|F_o| > 3\sigma(|F_o|)$, 2421 unique ($R_{\rm int} = 0{\cdot}01$), absorption correction ($0{\cdot}880 < A < 0{\cdot}921$). The systematic absences, hkl with $h + k$ odd, show that the space group is $C2$, Cm or $C2/m$. The space group was assumed to be $C2$ because this compound has an optically active ligand and the crystal structure should not have mirror symmetry. Structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Absolute structure was assigned with reference to the known absolute configuration of *R*,*R*-chxn moieties. Two independent acetone molecules and all H atoms except for the acetone H atoms were revealed by difference synthesis. Non-H atoms were refined anisotropically and H atoms isotropically by block-diagonal least squares using *UNICS*III computation program system (Sakurai & Kobayashi, 1979). $\sum w\big||F_o| - |F_c|\big|^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0{\cdot}015|F_o|)^2$, final $R = 0{\cdot}045$, $wR = 0{\cdot}063$, $S = 2{\cdot}66$ for 2421 unique reflections.* Reflection/parameter ratio 3·4, $\Delta/\sigma < 0{\cdot}2$, $-0{\cdot}25 \le \Delta\rho \le 0{\cdot}83$ e Å^{-3}. Complex neutral-atom scattering factors from *International Tables for X-ray Crystal-*

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44881 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* (×10⁴) *and equivalent isotropic temperature factors* (*Hamilton*, 1959)

	x	y	z	B_{eq}(Å^2 × 10)
Ti(1)	7969 (1)	10000*	7235 (1)	26
Cl(1)	8253 (1)	11893 (2)	6703 (1)	42
O(0)	7583 (2)	8770 (6)	7564 (2)	30
O(1)	8616 (2)	10550 (5)	8023 (2)	34
O(2)	8326 (2)	8700 (5)	6873 (2)	35
N(1)	7318 (2)	11514 (6)	7347 (2)	26
N(2)	7066 (2)	9849 (6)	6375 (2)	26
C(1)	8006 (3)	11779 (8)	8490 (3)	26
C(2)	8558 (3)	11035 (8)	8533 (3)	32
C(3)	9087 (3)	10819 (9)	9132 (3)	36
C(4)	9043 (3)	11358 (9)	9632 (3)	41
C(5)	8526 (4)	12137 (10)	9613 (3)	50
C(6)	7992 (3)	12319 (9)	9025 (3)	37
C(7)	7423 (3)	12032 (7)	7883 (3)	32
C(8)	7547 (3)	8426 (7)	5807 (3)	28
C(9)	8159 (3)	8154 (7)	6300 (3)	31
C(10)	8619 (3)	7319 (9)	6209 (4)	40
C(11)	8419 (4)	6695 (10)	5591 (4)	52
C(12)	7844 (4)	6987 (9)	5129 (3)	41
C(13)	7382 (4)	7803 (8)	5201 (3)	38
C(14)	7003 (3)	9206 (7)	5864 (3)	26
C(15)	6711 (3)	11849 (7)	6786 (3)	27
C(16)	6160 (3)	12516 (9)	6906 (3)	37
C(17)	5552 (3)	12804 (8)	6273 (4)	40
C(18)	5320 (3)	11489 (9)	5890 (3)	39
C(19)	5879 (3)	10790 (9)	5762 (3)	38
C(20)	6471 (3)	10516 (7)	6403 (3)	25
Ti(2)	7142 (1)	7383 (1)	7735 (1)	26
Cl(01)	6755 (1)	5304 (2)	8087 (1)	44
O(01)	6516 (2)	7079 (5)	6907 (2)	34
O(02)	6766 (2)	8490 (5)	8148 (2)	35
N(01)	7792 (2)	6032 (5)	7523 (2)	23
N(02)	7985 (2)	7088 (5)	8650 (2)	23
C(01)	7036 (3)	5548 (7)	6451 (3)	25
C(02)	6493 (3)	6391 (7)	6403 (3)	25
C(03)	5952 (4)	6535 (8)	5834 (3)	37
C(04)	5902 (4)	5862 (10)	5274 (4)	50
C(05)	6438 (4)	5016 (10)	5332 (3)	46
C(06)	6977 (3)	4835 (8)	5890 (3)	35
C(07)	7643 (3)	5438 (7)	6998 (3)	26
C(08)	7584 (3)	8703 (8)	9214 (3)	30
C(09)	6953 (3)	9012 (7)	8722 (3)	31
C(010)	6535 (3)	9936 (9)	8853 (3)	39
C(011)	6684 (4)	10463 (8)	9408 (4)	48
C(012)	7326 (4)	10136 (11)	9937 (4)	53
C(013)	7726 (4)	9265 (8)	9801 (4)	45
C(014)	8030 (3)	7738 (8)	9126 (3)	31
C(015)	8488 (3)	6010 (7)	8023 (3)	27
C(016)	8941 (3)	4867 (9)	7984 (3)	41
C(017)	9618 (3)	4930 (10)	8514 (3)	42
C(018)	9583 (3)	4893 (10)	9146 (3)	45
C(019)	9155 (3)	6109 (9)	9188 (3)	39
C(020)	8450 (3)	5996 (7)	8664 (3)	29
O(101)	5513 (3)	8245 (7)	14051 (3)	73
C(101)	5257 (5)	7824 (12)	13478 (6)	85
C(102)	5201 (5)	6265 (12)	13407 (5)	79
C(103)	5020 (5)	8792 (17)	12901 (4)	100
O(201)	9500 (3)	8657 (8)	10984 (3)	81
C(201)	9620 (4)	9229 (12)	11446 (5)	78
C(202)	9578 (6)	10782 (20)	11483 (5)	139
C(203)	9857 (6)	8577 (15)	12112 (7)	105

* This parameter was used to define the unit-cell origin along *y* and is listed without e.s.d.

lography (1974). Table 1 gives atomic coordinates and Table 2 gives bond distances and angles involving Ti atoms. Molecular structure and numbering scheme are shown in Fig. 1. Except for *R,R*-chxn moieties, this binuclear complex has a pseudo center of symmetry at the bridging O(0) atom whose x and z coordinates nearly equal 3/4 which gives pseudo structural symmetry $C2/c$ (see Fig. 2). This can be expected from the reflection data. The mean $|F_o|$ for 115 $h0l$ observed reflections with l odd is about half of that for 175 $h0l$ reflections with l even.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Ti(1)–Cl(1)	2·437 (3)	O(0)–Ti(2)	1·798 (6)
Ti(1)–O(0)	1·814 (6)	Ti(2)–Cl(01)	2·453 (3)
Ti(1)–O(1)	1·870 (4)	Ti(2)–O(01)	1·868 (4)
Ti(1)–O(2)	1·867 (6)	Ti(2)–O(02)	1·859 (6)
Ti(1)–N(1)	2·145 (6)	Ti(2)–N(01)	2·151 (6)
Ti(1)–N(2)	2·159 (4)	Ti(2)–N(02)	2·183 (4)
Cl(1)–Ti(1)–O(0)	167·6 (2)	O(0)–Ti(2)–Cl(01)	168·9 (2)
Cl(1)–Ti(1)–O(1)	92·2 (1)	O(0)–Ti(2)–O(01)	96·8 (2)
Cl(1)–Ti(1)–O(2)	90·9 (2)	O(0)–Ti(2)–O(02)	95·7 (2)
Cl(1)–Ti(1)–N(1)	83·7 (2)	O(0)–Ti(2)–N(01)	85·1 (2)
Cl(1)–Ti(1)–N(2)	84·9 (1)	O(0)–Ti(2)–N(02)	89·8 (2)
O(0)–Ti(1)–O(1)	93·8 (2)	Cl(01)–Ti(2)–O(01)	90·6 (1)
O(0)–Ti(1)–O(2)	97·2 (2)	Cl(01)–Ti(2)–O(02)	89·6 (2)
O(0)–Ti(1)–N(1)	85·7 (3)	Cl(01)–Ti(2)–N(01)	87·2 (1)
O(0)–Ti(1)–N(2)	86·3 (2)	Cl(01)–Ti(2)–N(02)	80·8 (1)
O(1)–Ti(1)–O(2)	110·1 (2)	O(01)–Ti(2)–O(02)	109·3 (2)
O(1)–Ti(1)–N(1)	87·7 (2)	O(01)–Ti(2)–N(01)	86·6 (2)
O(1)–Ti(1)–N(2)	163·5 (2)	O(01)–Ti(2)–N(02)	161·5 (2)
O(2)–Ti(1)–N(1)	161·7 (2)	O(02)–Ti(2)–N(01)	163·8 (2)
O(2)–Ti(1)–N(2)	86·3 (2)	O(02)–Ti(2)–N(02)	87·1 (2)
N(1)–Ti(1)–N(2)	75·8 (2)	N(01)–Ti(2)–N(02)	76·7 (2)
Ti(1)–O(0)–Ti(2)	168·3 (3)		

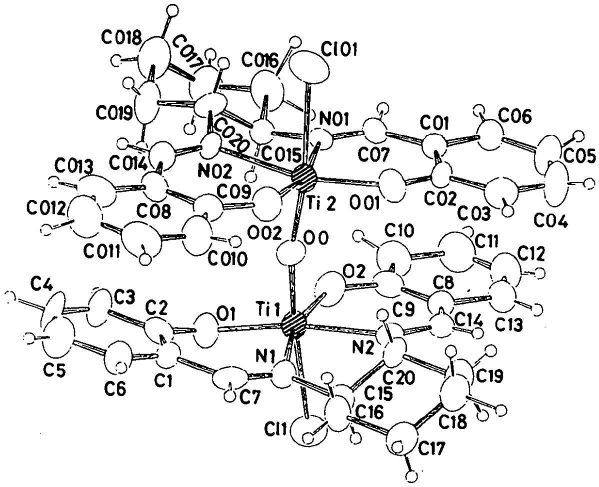

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule with thermal ellipsoids scaled at the 50% probability level. H atoms are represented by circles of radius 0·08 Å.

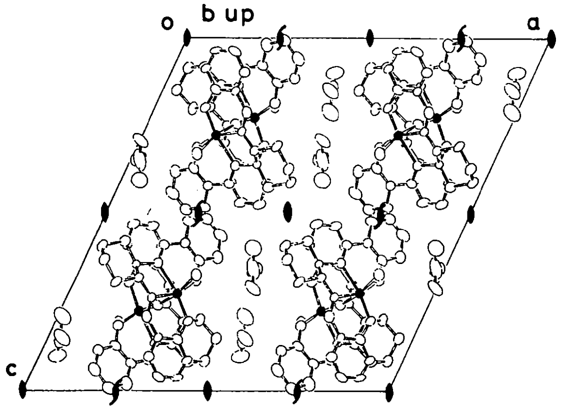

Fig. 2. Projection of crystal structure along **b**.

Related literature. The title compound catalyzes asymmetric oxidation of methyl phenyl sulfide to give (*R*)-methyl phenyl sulfoxide (Nakajima, Sasaki, Kojima, Aoyama, Ohba, Saito & Fujita, 1987). As far as we know, the structure of no other binuclear Ti–Schiff-base complex has been determined. The Ti^{III}–(Pasquali, Marchetti, Landi & Floriani, 1978) and Ti^{IV}–(Gilli, Cruickshank, Beddoes & Mills, 1972) Schiff-base complexes reported are mononuclear. The geometry of the Fe—O—Fe bridge in binuclear Fe^{III}–Schiff-base complexes was discussed by Davies & Gatehouse (1973).

References

Davies, J. E. & Gatehouse, B. M. (1973). *Acta Cryst.* B**29**, 2651–2658.

Gilli, G., Cruickshank, D. W. J., Beddoes, R. L. & Mills, O. S. (1972). *Acta Cryst.* B**28**, 1889–1893.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Nakajima, K., Sasaki, C., Kojima, M., Aoyama, T., Ohba, S., Saito, Y. & Fujita, J. (1987). *Chem. Lett.* pp. 2189–2192.

Pasquali, M., Marchetti, F., Landi, A. & Floriani, C. (1978). *J. Chem. Soc. Dalton Trans.* pp. 545–549.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

Acta Cryst. (1988). C**44**, 1311–1313

Structure d'une Nouvelle Variété de Di-μ-chloro-bis[(aza-4 azonia-1 bicyclo[2.2.2]octane)dichloromanganèse(II)]

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(*Reçu le* 4 *janvier* 1988, *accepté le* 18 *mars* 1988)

Abstract. $[Mn_2Cl_6(C_6H_{13}N_2)_2]$, $M_r = 548{\cdot}96$, orthorhombic, $Pbca$, $a = 12{\cdot}078\,(2)$, $b = 14{\cdot}218\,(2)$, $c = 12{\cdot}169\,(2)$ Å, $V = 2089{\cdot}6\,(9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}78\,(2)$, $D_x = 1{\cdot}745$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}94$ mm^{-1}, $F(000) = 1112$, $T = 294\,(1)$ K, $R = 0{\cdot}024$ for 1837 independent observed reflections. This compound is a modification of the monoclinic $P2_1/n$ complex [Viossat, Khodadad & Rodier (1988). *Acta Cryst.* C**44**, 825–828]. Its dimeric molecule also has a centre of symmetry, two Mn—Cl—Mn bridges and the coordination polyhedron of each Mn atom is a trigonal bipyramid. It differs from the molecule of the monoclinic variety by having larger distances from the N atoms to the plane of the two Mn—Cl—Mn bridges and by having greater N—C—C—N torsional angles, which prevents its description in terms of C_{2h} symmetry. In both forms, the molecules are linked together by N—H···Cl and C—H···Cl hydrogen bonds.

Partie expérimentale. Cristallisation lente obtenue par diffusion de vapeurs d'acétone dans la solution méthanolique. Masse volumique par flottaison. Cristal parallélépipédique: 0,25 × 0,35 × 0,40 mm. Dimensions de la maille déterminées sur monocristal avec 25 réflexions telles que $9{,}41 \le \theta \le 20{,}62°$. Diffractomètre Enraf–Nonius CAD-4. Scan $\theta/2\theta$ d'amplitude $s(°) = 0{,}65 + 0{,}35\,\text{tg}\theta$; $2 \le \theta \le 28°$; $0 \le h \le 15$, $0 \le k \le 18$, $0 \le l \le 16$. Réflexions de contrôle: 362, $\bar{4}\bar{4}2$ et $\bar{6}2\bar{3}$. $\sigma(I)/I$ moyen (contrôle): 0,0030. Diminution de I: 1,2%. 2514 réflexions indépendantes mesurées, 677 réflexions inobservées ($F_o \le F_{o,\max}/30$). Corrections d'absorption selon Walker & Stuart (1983). Valeurs maximale et minimale du coefficient de correction: 1,144 et 0,787. Programme *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) et série de Fourier des ΔF. Affinement basé sur les F. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974) corrigés des f' et f''. Paramètres affinés: x, y, z de tous les atomes et β_{ij} de Mn, Cl, N et C. B de chaque H laissé fixe et pris égal à $B_{\text{éq}}$ de l'atome porteur augmenté de 1 Å^2. $R = 0{,}024$, $wR = 0{,}019$, $w = 3F_o/F_{o,\max}$ lorsque $F_o <$

0108-2701/88/071311-03\$03.00