

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H11'...O1'	0.76 (3)	2.14 (3)	2.895 (4)	172 (5)
O1W—H12'...O3	0.74 (3)	2.37 (4)	3.061 (6)	157 (5)

Symmetry code: (i) $1 - x, 1 - y, -z$.

Water H atoms were refined with O—H distance restraints (command *SADI* in *SHELXL93*; Sheldrick, 1993) and methyls were refined as rigid groups, with other H atoms riding.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL93*.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1410). Services for accessing these data are described at the back of the journal.

References

- Armand, M., Baret, P., Chautemps, P. & Pierre, J.-L. (1981). *J. Am. Chem. Soc.* **103**, 2986–2988.
- Boekelheide, V., Eaton, B., Hanson, A. W. & Kang, H. C. (1985). *J. Am. Chem. Soc.* **107**, 1979–1985.
- Bubenitschek, P., Heitzler, F. R., Hopf, H. & Jones, P. G. (1995). *Chem. Ber.* **128**, 1079–1082.
- Cheung, L. D., Greene, F. D., Majeste, R., Trefonas, L. M. & Viavattene, R. L. (1974). *J. Am. Chem. Soc.* **96**, 4342–4343.
- Clardy, J. C., Haley, G. J., Matz, J. R., McMurry, J. E. & Mitchell, J. (1986). *J. Am. Chem. Soc.* **108**, 515–516.
- Cohen-Addad, C., Baret, P., Chautemps, P. & Pierre, J.-L. (1983). *Acta Cryst.* **C39**, 1346–1349.
- Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Gloe, K., Gross, J., Harder, G., Stephan, H. & Vögtle, F. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 481–484.
- Herges, R., Jones, P. G. & Kammermeier, S. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 2669–2671.
- Herges, R. & Kammermeier, S. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 417–419.
- Iijima, S. (1991). *Nature*, **354**, 56–58.
- Jones, P. G., Bubenitschek, P., Heitzler, F. R. & Hopf, H. (1996). *Acta Cryst.* **C52**, 1380–1384.
- Jones, P. G., Heitzler, F. R. & Hopf, H. (1996). *Acta Cryst.* **C52**, 1384–1388.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994a). *XEMP. Empirical Absorption Correction Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994b). *XP. Interactive Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). **C54**, 1081–1083

Manganese(II) Triphenylacetate Hydrate, a Manganese(II) Complex with a Chain Structure

TAMMY S. YAUKEY,^a OMAR W. STEWARD*^a AND SHIH-CHI CHANG^b

^aDepartment of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA, and ^bDepartment of Physics, Duquesne University, Pittsburgh, PA 15282, USA. E-mail: steward@duq3.cc.duq.edu

(Received 13 August 1997; accepted 23 February 1998)

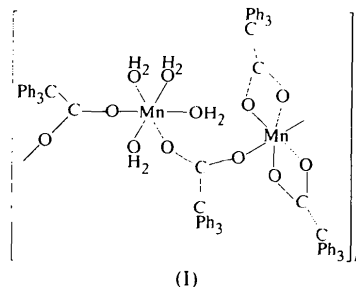
Abstract

The crystal structure of *catena*-poly[[tetraaqua-2κ⁴O-μ-triphenylacetato-1:2κ²O:O'-bis(triphenylacetato)-1κ⁴O,O'-dimanganese(II)]-μ-triphenylacetato-2κO:1'κO'], [Mn₂(C₂₀H₁₅O₂)₄(H₂O)₄]_n, was determined at 294 K by single-crystal X-ray diffraction. This compound has a chain structure with repeating dimeric units containing two crystallographically independent Mn^{II} atoms bridged by *sym-sym*-(μ-triphenylacetato-O,O') groups *via cis* positions.

Comment

Bridged metal carboxylates are of interest since the reactive site in many enzyme systems contain these structural features (Holm *et al.*, 1996).

Manganese(II) triphenylacetate hydrate, (I), has a chain structure. The repeating dimeric unit contains two crystallographically independent Mn^{II} atoms bridged by *sym-sym*-(μ-triphenylacetato-O,O') groups *via cis* positions; the Mn1 atom is bonded to two chelating



triphenylacetato groups, while Mn2 is bonded to four aqua ligands. The H atoms of the aqua ligands were located on structural refinement (Fig. 1). The Mn...Mn distances are Mn1...Mn2 4.5275 (7) and Mn1...Mn2' 4.7210 (7) Å. There are no inter-chain O...O distances less than 3.313 (5) Å. The only important intra-chain distance where a hydrogen bond almost certainly occurs is between the O4 atom of a chelating acetato ligand and the O9 atom of a ligated water molecule [2.693 (3) Å].

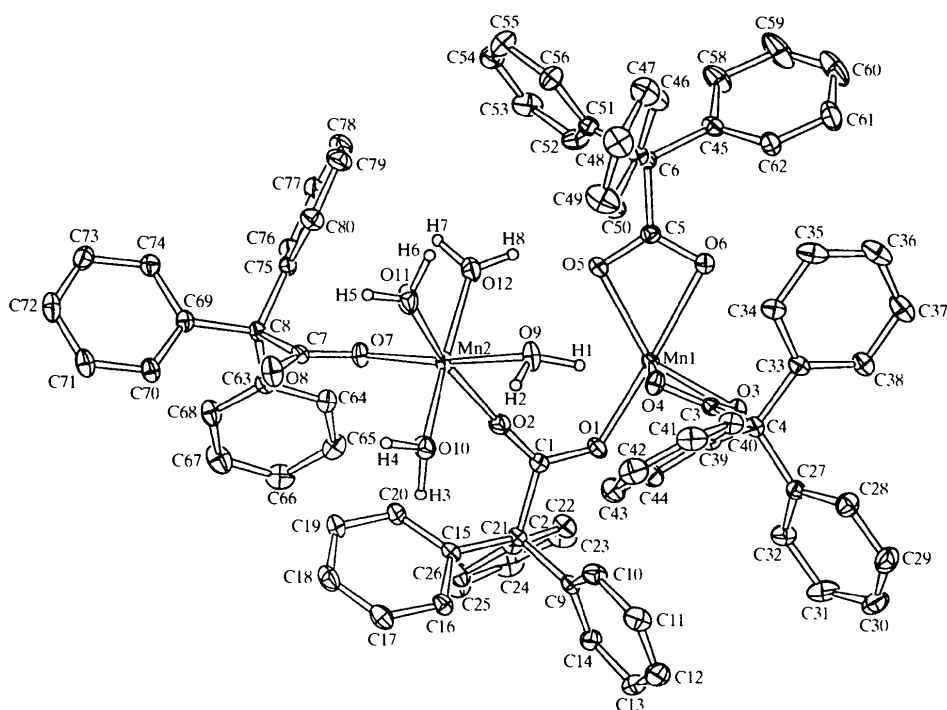
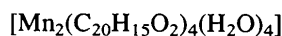


Fig. 1. Perspective drawing showing the chain structure of manganese(II) triphenylacetate hydrate, with displacement ellipsoids shown at the 20% probability level. The H atoms of the phenyl groups have been omitted for clarity.

The carboxylate stretching frequencies (IR crystalline solid) of the triphenylacetato ligands, both bridging and chelating, are of interest. The symmetrical stretch ($\bar{\nu}_{\text{sym}}$ 1379 cm^{-1}) is not unusual and shows only very slight shoulders. However, the asymmetric stretch occurs over a considerable range ($\bar{\nu}_{\text{asym}}$ $1511\text{--}1642\text{ cm}^{-1}$) and is multi-structured with a peak at 1563 cm^{-1} and a broad shoulder at $ca\ 1590\text{ cm}^{-1}$. It would be difficult to assign these absorptions to bridging and chelating carboxyl groups without applying isotopic substitution since the O—C—O angles of these groups vary over a considerable range ($116.1\text{--}123.7^\circ$) and cannot be grouped by type, *cf.* Table 1 (Mehrotra & Bohra, 1983).

Experimental

The title complex, $[\text{Mn}_2(\text{O}_2\text{CCPh}_3)_4(\text{H}_2\text{O})_4]_n$, was prepared by a method similar to that reported previously for copper(II)-carboxylate complexes (Steward *et al.*, 1986). Triphenylacetic acid (1.54 g, 6.94 mmol) was dissolved in 0.25 M NaOH (100 ml) with stirring. The solution was filtered and three drops of phenolphthalein indicator were added. Nitric acid (*ca* 1 M) was added from a buret until the end point was reached. Manganese(II) nitrate (50% solution, 1.3 ml, 6.9 mmol of Mn^{II}) was added yielding a white precipitate. The precipitate was separated by filtration and allowed to dry overnight yielding 1.86 g of a white solid (92% yield). The complex (0.5 g) was dissolved in absolute ethanol with heating on a

steam bath. The resulting solution was filtered and allowed to evaporate slowly yielding colorless crystals. Calculated for $\text{C}_{80}\text{H}_{68}\text{Mn}_2\text{O}_{12}$: C 72.17, H 5.15%; found: C 71.81, H 5.02%.

Crystal data



$M_r = 1331.29$

Triclinic

$P\bar{1}$

$a = 14.766(2)\ \text{\AA}$

$b = 24.223(5)\ \text{\AA}$

$c = 9.239(1)\ \text{\AA}$

$\alpha = 94.74(1)^\circ$

$\beta = 96.72(1)^\circ$

$\gamma = 87.19(1)^\circ$

$V = 3268.2(10)\ \text{\AA}^3$

$Z = 2$

$D_x = 1.353\ \text{Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107\ \text{\AA}$

Cell parameters from 25

reflections

$\theta = 30.1\text{--}38.9^\circ$

$\mu = 0.452\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Tetragonal

$0.40 \times 0.10 \times 0.10\ \text{mm}$

Colorless

Data collection

Rigaku AFC-7R diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (TEXSAN;

Molecular Structure

Corporation, 1992)

$T_{\text{min}} = 0.835$, $T_{\text{max}} = 0.999$

15 569 measured reflections

14 988 independent

reflections

8682 reflections with

$I > 3\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\text{max}} = 27.50^\circ$

$h = 0 \rightarrow 19$

$k = -31 \rightarrow 31$

$l = -12 \rightarrow 11$

3 standard reflections

every 150 reflections

intensity decay: 3.77%

RefinementRefinement on F $R = 0.048$ $wR = 0.052$ $S = 1.94$

8682 reflections

847 parameters

H atoms not refined

Weighting scheme based

on measured s.u.'s;

$$w = 4F^2/\sigma^2(F^2)$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.71 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.Steward, O. W., McAfee, R. C., Chang, S.-C., Piskor, S. R., Schreiber, W. J., Jury, C. F., Taylor, C. E., Pletcher, J. F. & Chen, S.-C. (1986). *Inorg. Chem.* **25**, 771–777.*Acta Cryst.* (1998). **C54**, 1083–1085Table 1. Selected geometric parameters (\AA , $^\circ$)

Mn1—O1	2.102 (2)	O3—C3	1.266 (4)
Mn1—O3	2.228 (2)	O4—C3	1.245 (4)
Mn1—O5	2.226 (2)	O5—C5	1.267 (4)
Mn1—O8'	2.065 (2)	O6—C5	1.241 (4)
Mn2—O2	2.100 (3)	O7—C7	1.246 (4)
Mn2—O7	2.127 (2)	O8—C7	1.233 (4)
Mn2—O10	2.210 (3)	C1—C2	1.579 (4)
Mn2—O11	2.174 (3)	C3—C4	1.564 (4)
Mn2—O12	2.189 (3)	C5—C6	1.554 (4)
O1—C1	1.261 (4)	C7—C8	1.589 (4)
O2—C1	1.228 (4)		
O1—Mn1—O3	95.84 (9)	O10—Mn2—O11	88.4 (1)
O1—Mn1—O5	120.77 (9)	O10—Mn2—O12	170.2 (1)
O1—Mn1—O8'	98.3 (1)	O11—Mn2—O12	84.6 (1)
O3—Mn1—O5	132.51 (9)	Mn1—O1—C1	130.5 (2)
O3—Mn1—O8'	97.73 (9)	Mn2—O2—C1	167.5 (3)
O5—Mn1—O8'	104.9 (1)	Mn1—O3—C3	92.9 (2)
O2—Mn2—O7	97.5 (1)	Mn1—O5—C5	95.1 (2)
O2—Mn2—O10	88.22 (10)	Mn2—O7—C7	136.0 (2)
O2—Mn2—O11	165.8 (1)	Mn1 ⁱⁱ —O8—C7	168.5 (3)
O2—Mn2—O12	97.0 (1)	O1—C1—O2	123.7 (3)
O7—Mn2—O10	104.77 (10)	O3—C3—O4	121.0 (3)
O7—Mn2—O11	96.7 (1)	O5—C5—O6	118.6 (3)
O7—Mn2—O12	82.90 (10)	O7—C7—O8	124.4 (3)

Symmetry codes: (i) $x, y, 1 + z$; (ii) $x, y, z - 1$.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Financial support from the Kresge Foundation is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1373). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.
- Holm, R. H., Kennepohl, P. & Solomon, E. I. (1996). *Chem. Rev.* **96**, 2239–2314, and references therein.
- Mehrotra, R. C. & Bohra, R. (1983). *Metal Carboxylates*, pp. 48–60, and references therein. New York: Academic Press.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Absolute Configuration of (+)₅₈₉-(4,4'-Dimethoxy-2,2'-bipyridine 1,1'-dioxide-O,O')bis(ethylenediamine-N,N')cobalt(III) Triperchlorate

HIDEAKI KANNO,^a SHUNJI UTSUNO,^a JUNNOSUKE FUJITA^b AND KINYA IJIMA^a

^aDepartment of Chemistry, Faculty of Science, Shizuoka University, 836 Oya, Shizuoka 422, Japan, and ^bDivision of Natural Sciences, International Christian University, Osawa, Mitaka 181, Japan. E-mail: sckijji@sci.shizuoka.ac.jp

(Received 21 November 1997; accepted 17 February 1998)

Abstract

The complex ion of the title molecule, (+)₅₈₉-[Co(C₂H₈N₂)₂(C₁₂H₁₂N₂O₄)](ClO₄)₃, has twofold symmetry and the absolute configuration is Λ . The seven-membered chelate ring of the 4,4'-dimethoxy-2,2'-bipyridine 1,1'-dioxide ligand adopts a δ chiral skew conformation, which forms a *lel* structure in the complex ion. The dihedral angle between the two pyridine rings is 61.2 (2)°, and the O—Co—O bite angle is 91.3 (2)°. The ethylenediamine chelates take a δ -*gauche* conformation in the complex ion.

Comment

2,2'-Bipyridine 1,1'-dioxide (bpdo) forms a skewed seven-membered chelate ring with a metal ion (Al-Karaghoulis *et al.*, 1978; Alcock & Roberts, 1987; Koman *et al.*, 1991; Baran *et al.*, 1991). Since the skew conformation produces a pair of enantiomers, δ and λ , a tris(bpdo) complex has four possible racemic pairs of diastereomers. Recently, it was reported that a tris[4,4'-(MeO)₂bpdo]chromium(III) complex gave two of four possible diastereomers, where 4,4'-(MeO)₂bpdo is the 4,4'-dimethoxy derivative of bpdo (Kanno *et al.*, 1996). However, the molecular structures of optically active complexes with bpdo have not been reported. A new bis(en)cobalt(III) complex with 4,4'-(MeO)₂bpdo was thus prepared, where en is ethylenediamine. The complex, (I), was found to form only one diastereomer in solution (¹³C NMR spectrum), though the complex has two