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Key indicators

Single-crystal X-ray study

 $T = 298\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$ R factor = 0.055 wR factor = 0.193

Data-to-parameter ratio = 23.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Di- μ -methoxo- $\kappa^4\text{O}:\text{O}$ -bis[bis(1,3-diphenyl-
propane-1,3-dionato- $\kappa^2\text{O},\text{O}'$)chromium(III)]

The title compound, $[\text{Cr}_2(\text{CH}_3\text{O})_2(\text{C}_{15}\text{H}_{11}\text{O}_2)_4]$, was obtained from the reaction of $[\text{CrCl}_3(\text{C}_4\text{H}_8\text{O})_3]$ with 1,3-diphenylpropane-1,3-dione and sodium methoxide in anhydrous methanol. Its structure consists of discrete molecules, in which two centrosymmetrically related chromium(III) ions are bridged by two methoxide ligands and complete their octahedral coordination geometry with O atoms from β -diketonate molecules acting as ancillary ligands.

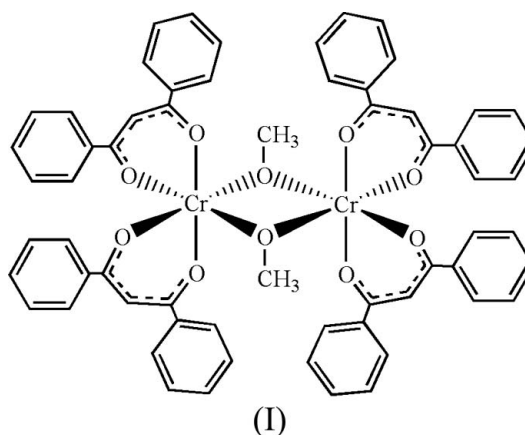
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Comment

Recently, increasing attention has been focused on using β -diketonates as ancillary ligands in the synthesis of high-nuclearity complexes with magnetic properties. Their bonding ability can be exploited in one-pot alkoxide-promoted aggregation reactions to obtain compounds with appealing structures (Caneschi *et al.*, 1995), as well as unusual physical properties, like quantum tunnelling of the magnetization and magnetic hysteresis of molecular origin (Barra *et al.*, 1999). Among the suitable β -diketonate ligands, 1,3-diphenylpropane-1,3-dione (Hdbm) has proved to be particularly versatile and has been successfully employed in the synthesis of various iron(III) (Caneschi *et al.*, 1995; Abbati *et al.*, 2000) and manganese(II,III) alkoxo-clusters (Abbati *et al.*, 1998). As part of a current effort to isolate novel high-spin compounds, the reactivity of Hdbm with chromium(III) and alkaline alkoxides has been explored. The synthesis and structure of the title compound, (I), is reported here.



as two centrosymmetrically related $[\text{Cr}(\text{dbm})_2]$ units bridged by two methoxide ligands [$\text{Cr}1 \cdots \text{Cr}1^i = 3.0216(13) \text{ \AA}$; symmetry code: (i) $-x, 1 - y, 1 - z$]. The two chromium(III) ions show a slightly distorted octahedral coordination geometry provided by the O atoms from the *cis*-methoxide as well as bidentate dbm anionic ligands, with Cr–O bond lengths falling in the narrow range 1.945 (3)–1.967 (2) \AA (see Table 1) and *trans* and *cis* O–Cr–O angles values in the ranges 173.17 (11)–174.94 (11) and 85.04 (10)–95.63 (11) $^\circ$, respectively. A notable exception is the $\text{O}5 - \text{Cr}1 - \text{O}5^i$ angle, which shows a significantly more acute value of 79.32 (11) $^\circ$, leading to an $\text{O}5 \cdots \text{O}5^i$ distance of 2.505 (5) \AA . The Cr_2O_2 ring is planar by symmetry, with the C31 and C31 i methoxy C atoms displaced out of the plane of the four atoms by 0.760 (6) \AA (symmetry code as in Table 1).

The structure of the dbm anionic ligands closely resembles that shown in the related $[\text{M}_2(\text{OCH}_3)_2(\text{dbm})_4]$ ($M = \text{Fe}, \text{Mn}; \text{Le Gall et al., 1997; Abbati et al., 1998}$) compounds. The five-membered chelate rings are essentially planar, with maximum deviations from the least-squares planes defined by O1/C1/C3/C4/O2 and O3/C16/C18/C17/O4 of 0.021 (3) \AA (for C2) and 0.030 (3) \AA for (C17), respectively, a dihedral angle between the planes of 61.1 (2) $^\circ$, and O \cdots O ‘bite’ distances of 2.755 (3) and 2.762 (3) \AA , respectively. The chromium(III) ions show considerable deviations from the chelating planes, with deviations of 0.474 (4) and 0.412 (4) \AA .

Analysis of the crystal structure shows no evidence of significant intermolecular interactions.

The atoms belonging to phenyl rings show relatively high values of U_{eq} , indicating that some freedom of packing may be possible in these parts of the molecule. This behavior may explain the short C–C distances observed in the C25–C30 phenyl ring (Albertsson *et al.*, 1980).

Although some alkoxo-supported chromium(III) dinuclear complexes with dipivaloylmethane (Fischer *et al.*, 1984), acetylacetonate (Fischer *et al.*, 1982) or halogen-containing β -diketonates (Estes *et al.*, 1976; Estes *et al.*, 1977) are known, to my knowledge complex (I) is the first example of a polynuclear alkoxo-bridged chromium(III) complex containing 1,3-diphenylpropane-1,3-dione so far reported. In view of the structural relation existing among low-nuclearity alkoxo-bridged complexes and high-nuclearity magnetic clusters containing $[\text{M}(\text{OCH}_3)(\text{dbm})_2]$ units ($M = \text{Fe}$ and $\text{Mn}; \text{Le Gall et al., 1997; Abbati et al., 1998}$), complex (I) is likely to represent a promising ‘building block’ for the synthesis of discrete higher nuclearity chromium(III) systems.

Experimental

All operations were carried out with strict exclusion of moisture. Methanol was dried by treatment with Mg/I_2 and distilled (Vogel, 1959). The Cr^{III} complex $[\text{CrCl}_3(\text{C}_6\text{H}_5\text{O})_3]$ (2 mmol), prepared according to the literature method (Herwig & Zeiss, 1958), was dissolved in methanol (6 ml). A methanol solution (25 ml) of Hdbm (2 mmol) and CH_3ONa (8 mmol) was then added dropwise with stirring. The resulting green suspension was stirred for 4 h at room

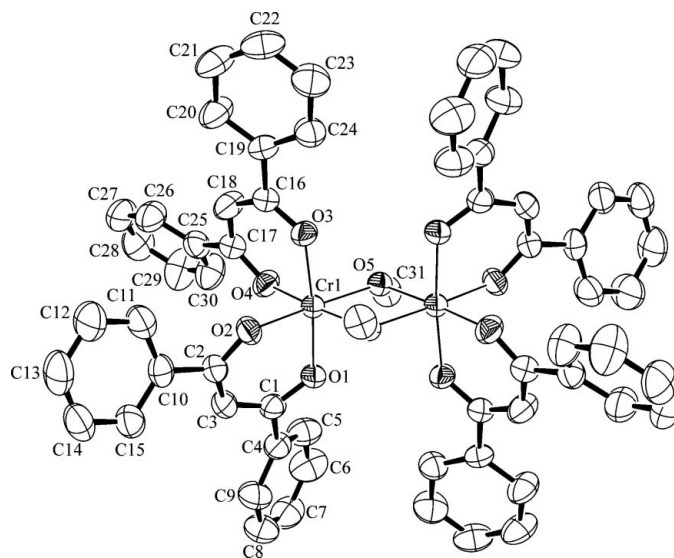


Figure 1

The molecular structure of (I), showing the atom-labeling scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry code for unlabeled atoms: $-x, 1 - y, 1 - z$.]

temperature, and the light-green precipitate was collected by filtration, washed with methanol and treated under stirring with chloroform (60 ml). The solution was filtered to remove some undissolved material and layered with methanol. Air-stable rod-like brown-green crystals formed in about one week. Analysis found: C 70.35, H 4.35%; calculated for $\text{C}_{62}\text{H}_{46}\text{Cr}_2\text{O}_{10}$: C 70.31, H 4.76%.

Crystal data

$[\text{Cr}_2(\text{CH}_3\text{O})_2(\text{C}_{15}\text{H}_{11}\text{O}_2)_4]$
 $M_r = 1059.02$
 Triclinic, $P\bar{1}$
 $a = 9.618(2) \text{ \AA}$
 $b = 10.905(2) \text{ \AA}$
 $c = 13.030(2) \text{ \AA}$
 $\alpha = 79.16(2)^\circ$
 $\beta = 87.389(10)^\circ$
 $\gamma = 81.635(10)^\circ$
 $V = 1327.7(4) \text{ \AA}^3$
 $Z = 1$
 $D_x = 1.324 \text{ Mg m}^{-3}$

$D_m = 1.33(1) \text{ Mg m}^{-3}$
 D_m measured by flotation in $\text{MeOH}/\text{CHBr}_3$
 Mo $K\alpha$ radiation
 Cell parameters from 20 reflections
 $\theta = 8.0\text{--}14.2^\circ$
 $\mu = 0.47 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Rod, green-brown
 $0.40 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.835, T_{\text{max}} = 0.933$
 8032 measured reflections
 7716 independent reflections
 2954 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -15 \rightarrow 15$
 $l = 0 \rightarrow 18$
 2 standard reflections
 frequency: 60 min
 intensity decay: 4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.193$
 $S = 0.94$
 7716 reflections
 334 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.091P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cr1—O2	1.945 (3)	O1—O2	2.755 (3)
Cr1—O4	1.955 (3)	O2—C2	1.271 (4)
Cr1—O3	1.956 (2)	O3—C16	1.263 (4)
Cr1—O5 ⁱ	1.958 (2)	O3—O4	2.762 (3)
Cr1—O1	1.963 (2)	O5—C31	1.420 (4)
Cr1—O5	1.967 (2)	O5—O5 ⁱ	2.505 (5)
O1—C1	1.272 (4)		
O2—Cr1—O4	91.08 (11)	O3—Cr1—O1	173.86 (10)
O2—Cr1—O3	87.01 (11)	O5 ⁱ —Cr1—O1	92.19 (10)
O4—Cr1—O3	89.86 (10)	O2—Cr1—O5	93.97 (11)
O2—Cr1—O5 ⁱ	173.17 (11)	O4—Cr1—O5	174.94 (11)
O4—Cr1—O5 ⁱ	95.63 (11)	O3—Cr1—O5	90.61 (10)
O3—Cr1—O5 ⁱ	91.70 (10)	O5 ⁱ —Cr1—O5	79.32 (11)
O2—Cr1—O1	89.67 (10)	O1—Cr1—O5	94.77 (10)
O4—Cr1—O1	85.04 (10)	Cr1 ⁱ —O5—Cr1	100.68 (11)

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

All H atoms were positioned geometrically ($C-H = 0.93-0.96$ Å) and refined as riding atoms, with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$. The ratio of observed to unique reflections is low (38%), possibly as a result of the rather weak diffracting ability shown by the crystal used for the X-ray analysis.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR97* (Altomare, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

- Abbati, G. L., Caneschi, A., Cornia, A., Fabretti A. C. & Gatteschi, D. (2000). *Inorg. Chim. Acta*, **297**, 291–300.
- Abbati, G. L., Cornia, A., Fabretti A. C., Caneschi, A. & Gatteschi, D. (1998). *Inorg. Chem.* **37**, 3759–3766.
- Albertsson, J., Oskarsson, Å., Ståhl, K., Svensson, C. & Ymén, I. (1980). *Acta Cryst.* **B36**, 3072–3078.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Barra, A.-L., Caneschi, A., Cornia, A., Fabrizi de Biani, F., Gatteschi, D., Sangregorio, C., Sessoli, R. & Sorace, L. (1999). *J. Am. Chem. Soc.* **121**, 5302–5310.
- Caneschi, A., Cornia, A. & Lippard, S. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 467–469.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Estes, E., D., Scaringe, R., P., Hatfield, W. E. & Hodgson, D. J. (1976). *Inorg. Chem.* **15**, 1179–1182.
- Estes, E., D., Scaringe, R., P., Hatfield, W. E. & Hodgson, D. J. (1977). *Inorg. Chem.* **16**, 1605–1610.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fischer, E., R., Glerup, J., Hodgson, D. J. & Pedersen, E. (1982). *Inorg. Chem.* **21**, 3063–3066.
- Fischer, E., R., Hodgson, D. J. & Pedersen, E. (1984). *Inorg. Chem.* **23**, 4755–4758.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Herwig, W. & Zeiss, H. H. (1958). *J. Org. Chem.* **23**, 1404.
- Le Gall, F., Fabrizi de Biani, F., Caneschi, A., Cinelli, P., Cornia, A., Fabretti, A. C. & Gatteschi, D. (1997). *Inorg. Chim. Acta*, **262**, 123–132.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Vogel, A. I. (1959). *Practical Organic Chemistry*, 3rd ed. London: Longmans.