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# Syntheses and crystal structures of three [$M$(acac)$_2$(TMEDA)] complexes ($M$ = Mn, Fe and Zn)

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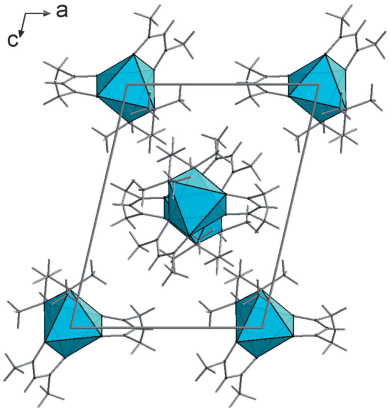
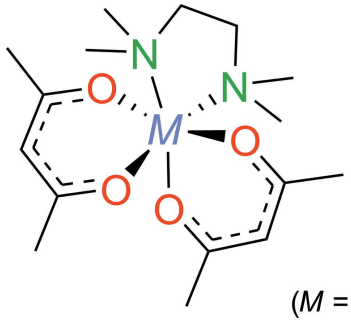
The complexes bis(acetylacetonato-$\kappa^2O,O'$)($N,N,N',N'$-tetramethylethylenediamine-$\kappa^2N,N'$)manganese(II), [Mn(C$_5$H$_7$O$_2$)$_2$(C$_6$H$_{16}$N$_2$)], bis(acetylacetonato-$\kappa^2O,O'$)($N,N,N',N'$-tetramethylethylenediamine-$\kappa^2N,N'$)iron(II), [Fe(C$_5$H$_7$O$_2$)$_2$-(C$_6$H$_{16}$N$_2$)], and bis(acetylacetonato-$\kappa^2O,O'$)($N,N,N',N'$-tetramethylethylenediamine-$\kappa^2N,N'$)zinc(II), [Zn(C$_5$H$_7$O$_2$)$_2$(C$_6$H$_{16}$N$_2$)], were synthesized from the reaction of the corresponding metal acetylacetonates [$M$(acac)$_2$(H$_2$O)$_2$] with $N,N,N',N'$-tetramethylethylenediamine (TMEDA) in toluene. Each of the complexes displays a central metal atom which is nearly octahedrally surrounded by two chelating acac and one chelating TMEDA ligand, resulting in an N$_2$O$_4$ coordination set. Despite the chemical similarity of the complex units, the packing patterns for compounds **1**–**3** are different and thus the crystal structures are not isotypic.

## 1. Chemical context

Pentane-2,4-dionate (acac) and ethylenediamine derivatives are amongst the most widely used chelate ligands in transition metal chemistry. The crystal structures of mixed complexes [$M$(acac)$_2$(TMEDA)] (TMEDA = $N,N,N',N'$-tetramethylethylenediamine) containing both types of ligands have been reported for several divalent metals, *e.g.* $M$ = V (Ma *et al.*, 1999), Co (Pasko *et al.*, 2004), Ni (Trimmel *et al.*, 2002; Zeller *et al.*, 2004) and Ru (Halbach *et al.*, 2012). The synthesis of [Zn(acac)$_2$(TMEDA)] was reported recently in conjunction with the Ru derivative but without crystal structure determination (Halbach *et al.*, 2012). Typically, [$M$(acac)$_2$(TMEDA)] complexes are used as valuable starting materials for the preparation of organometallic and coordination compounds (Kaschube *et al.* 1988; Nelkenbaum *et al.*, 2005; Albrecht *et al.*, 2019). Moreover, there is an increasing interest in [$M$(acac)$_2$(TMEDA)] and related [$M$(hfa)$_2$(TMEDA)] (hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) complexes as precursor materials for CVD deposition of Co$_3$O$_4$ (Pasko *et al.*, 2004), Fe$_2$O$_3$ (Barreca *et al.*, 2012) and MnF$_2$ (Malandrino *et al.*, 2012).




($M$ = Mn, Fe, Zn)

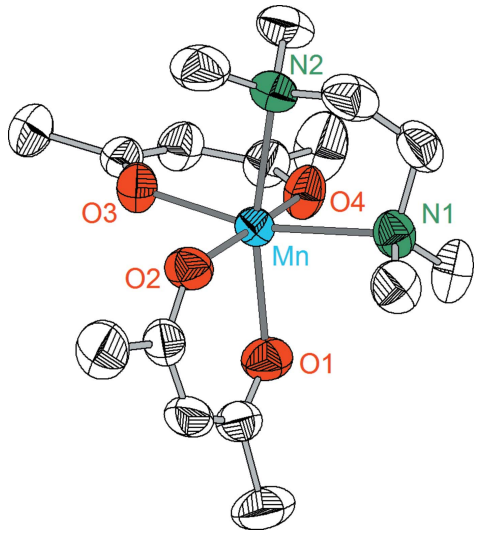



**Figure 1**
Molecular structure of complex **1** showing the labeling scheme. Displacement ellipsoids drawn at 50% probability level, H atoms are omitted.

Typically, [$M$(acac)$_2$(TMEDA)] complexes are synthesized from the reaction of the metal acetylacetonates with TMEDA. Following this procedure, we obtained the complexes [Mn(acac)$_2$(TMEDA)] (**1**), [Fe(acac)$_2$(TMEDA)] (**2**) and [Zn(acac)$_2$(TMEDA)] (**3**) from the corresponding dihydrates [$M$(acac)$_2$(H$_2$O)$_2$] and TMEDA in toluene as solvent. Recrystallization from *n*-hexane at 248 K afforded [Mn(acac)$_2$(TMEDA)] (**1**) as yellow, [Fe(acac)$_2$(TMEDA)] (**2**) as red–brown and [Zn(acac)$_2$(TMEDA)] (**3**) as colorless products. Determination of the magnetic moments for [Mn(acac)$_2$(TMEDA)] (5.7 B.M.) and [Fe(acac)$_2$(TMEDA)] (5.1 B.M.) indicates a high-spin configuration in both cases.

**Table 1**
Selected geometric parameters (Å, °) for **1**.

| | | | |
|---|---|---|---|
| Mn—O1 | 2.1271 (13) | Mn—O4 | 2.1365 (12) |
| Mn—O2 | 2.1500 (12) | Mn—N1 | 2.3643 (15) |
| Mn—O3 | 2.1375 (12) | Mn—N2 | 2.3560 (15) |
| | | | |
| O1—Mn—O2 | 83.61 (5) | O2—Mn—N2 | 90.36 (5) |
| O1—Mn—O3 | 107.00 (5) | O3—Mn—O4 | 83.78 (5) |
| O1—Mn—O4 | 93.25 (5) | O3—Mn—N1 | 165.43 (5) |
| O1—Mn—N1 | 86.01 (5) | O3—Mn—N2 | 90.61 (5) |
| O1—Mn—N2 | 161.29 (6) | O4—Mn—N1 | 89.07 (5) |
| O2—Mn—O3 | 89.71 (5) | O4—Mn—N2 | 94.95 (6) |
| O2—Mn—O4 | 171.63 (5) | N1—Mn—N2 | 77.34 (6) |
| O2—Mn—N1 | 98.41 (5) | | |

## 2. Structural commentary

Compounds **1**–**3** crystallize in the monoclinic system, space group $P2_1/n$ with $Z$ = 4. However, despite the similarity of the lattice parameters and the analogous molecular structures, complexes **1**–**3** are not isotypic. The crystal structures consist of discrete complex molecules [$M$(acac)$_2$TMEDA] in which the central metal atoms are coordinated nearly octahedrally by four oxygen atoms of two acac ligands and two nitrogen atoms of the TMEDA ligand (Figs. 1–3). Mn complex **1** exhibits Mn—O and Mn—N distances of 2.127 (1)–2.150 (1) Å and 2.356 (2)–2.364 (2) Å, respectively (Table 1). Similar geometric parameters have been reported for [Mn(acac)$_2$(H$_2$O)$_2$] [Mn—O: 2.123 (8)–2.142 (8) Å; Montgomery & Lingafelter, 1968], [Mn(acac)$_2$(1,10-phenanthroline)] [Mn—O: 2.116 (5)–2.152 (5) Å, Mn—N: 2.307 (5) Å; Stephens, 1977], [Mn(acac)$_2$(2,2′-bipyridine)] [Mn—O: 2.148 (2)–2.158 (2) Å, Mn—N: 2.283 (2)–2.288 (3) Å; van Gorkum *et al.*, 2005] or [Mn(hfa)$_2$(TMEDA)] [Mn—O: 2.139 (4)–2.178 (4) Å, Mn—N: 2.299 (5)—2.307 (5) Å; Malandrino *et al.*, 2012].

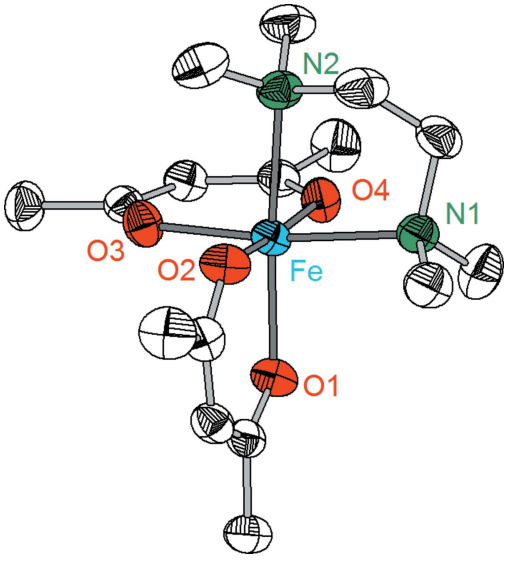



**Figure 2**
Molecular structure of complex **2** showing the labeling scheme. Displacement ellipsoids drawn at 50% probability level, H atoms are omitted.

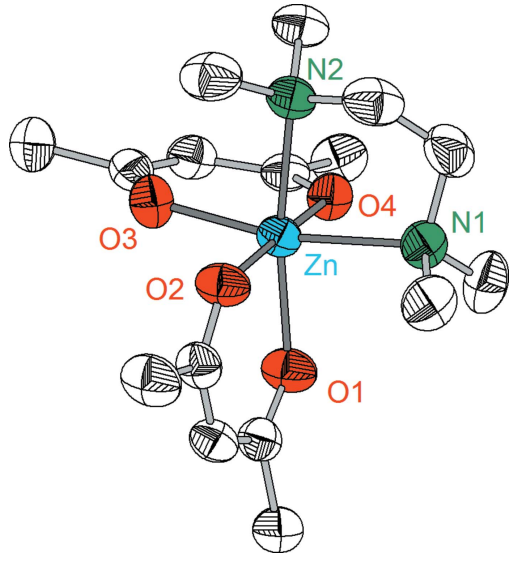



**Figure 3**
Molecular structure of complex **3** showing the labeling scheme. Displacement ellipsoids drawn at 50% probability level, H atoms are omitted.

**Table 2**
Selected geometric parameters (Å, °) for **2**.

| | | | |
|---|---|---|---|
| Fe—O1 | 2.0876 (10) | Fe—O4 | 2.0520 (9) |
| Fe—O2 | 2.0497 (10) | Fe—N1 | 2.3021 (12) |
| Fe—O3 | 2.0970 (10) | Fe—N2 | 2.3184 (12) |
| | | | |
| O1—Fe—O2 | 85.58 (4) | O2—Fe—N2 | 84.18 (4) |
| O1—Fe—O3 | 93.98 (4) | O3—Fe—O4 | 86.00 (4) |
| O1—Fe—O4 | 99.11 (4) | O3—Fe—N1 | 170.93 (4) |
| O1—Fe—N1 | 92.44 (4) | O3—Fe—N2 | 95.43 (4) |
| O1—Fe—N2 | 166.73 (4) | O4—Fe—N1 | 86.66 (4) |
| O2—Fe—O3 | 95.84 (4) | O4—Fe—N2 | 90.87 (4) |
| O2—Fe—O4 | 174.85 (4) | N1—Fe—N2 | 79.35 (4) |
| O2—Fe—N1 | 91.04 (5) | | |

**Table 3**
Selected geometric parameters (Å, °) for **3**.

| | | | |
|---|---|---|---|
| Zn—O1 | 2.0771 (12) | Zn—O4 | 2.0607 (10) |
| Zn—O2 | 2.0611 (11) | Zn—N1 | 2.2722 (13) |
| Zn—O3 | 2.0645 (11) | Zn—N2 | 2.2533 (13) |
| | | | |
| O1—Zn—O2 | 87.50 (4) | O2—Zn—N2 | 89.57 (5) |
| O1—Zn—O3 | 101.58 (5) | O3—Zn—O4 | 87.96 (4) |
| O1—Zn—O4 | 88.49 (4) | O3—Zn—N1 | 168.61 (5) |
| O1—Zn—N1 | 89.28 (5) | O3—Zn—N2 | 89.09 (5) |
| O1—Zn—N2 | 168.94 (5) | O4—Zn—N1 | 88.92 (5) |
| O2—Zn—O3 | 90.18 (5) | O4—Zn—N2 | 94.86 (5) |
| O2—Zn—O4 | 175.16 (4) | N1—Zn—N2 | 80.27 (5) |
| O2—Zn—N1 | 93.76 (5) | | |

The Fe—O and Fe—N distances in compound **2** [2.050 (1)–2.097 (1) Å and 2.302 (1)–2.318 (1) Å, respectively; Table 2] are on average shorter than the corresponding Mn—O and Mn—N distances in complex **1**. The Fe—O and Fe—N distances compare well with the data that have been observed in the compounds [Fe(acac)$_2$(H$_2$O)$_2$] [Fe—O: 2.034–2.041 Å; Tsodikov *et al.*, 1995], [Fe(hfa)$_2$(picoline)$_2$] [Fe—O: 2.057 (1) Å, Fe—N: 2.190 (3)–2.224 (3) Å; Novitchi *et al.*, 2017] or [Fe(hfa)$_2$(TMEDA)] [Fe—O: 2.064 (1)–2.094 (1), Fe—N: 2.229 (2) Å; Dickman *et al.*, 1998].

[Zn(acac)$_2$(TMEDA)] (**3**) displays Zn—O and Zn—N distances of 2.061 (1)–2.077 (1) and 2.253 (1)–2.272 (1) Å, respectively (Table 3). In comparison with the iron complex **2**, the average metal–oxygen distances and metal–nitrogen distances are slightly shortened. On the whole, the Zn—O and Zn—N distances in compound **3** are similar to those observed in the related compounds [Zn(acac)$_2$(H$_2$O)$_2$] [Zn—O: 2.032 (1)–2.049 (1) Å; Harbach *et al.*, 2003], [Zn(acac)$_2$(1,10-phenanthroline)] [Zn—O: 2.044 (1)–2.085 (1) Å, Zn—N: 2.196 (1) Å; Brahma *et al.*, 2008], [Zn(acac)$_2$(2,2′-bipyridine)] [Zn—O: 2.051 (1)–2.089 (1) Å, Zn—N: 2.197 (2)–2.208 (2) Å; Brahma *et al.*, 2008] or [Zn(hfa)$_2$(TMEDA)] [Zn—O: 2.103 (1)–2.126 (1) Å, Zn—N: 2.145 (1)–2.151 (1) Å; Ni *et al.*, 2005].

In general, the above-mentioned [*M*(hfa)$_2$(TMEDA)] (*M* = Mn, Fe, Zn) complexes exhibit shorter *M*—N distances than the corresponding [*M*(acac)$_2$(TMEDA)] complexes. This effect is probably due to the electron-withdrawing effect of the CF$_3$ groups of the hfa ligands.

The iron complex **2** displays a subtle elongation (0.041 Å) of the Fe—O bonds *trans* to the N atoms with respect to the Fe—O bonds *trans* to oxygen. A similar effect was observed for [Co(acac)$_2$(TMEDA)] (Pasko *et al.*, 2004). In the case of the Mn and Zn complexes **1** and **3**, the *trans* influence is negligible as reported for [Ni(acac)$_2$(TMEDA)] (Trimmel *et al.*, 2002) and [Ru(acac)$_2$(TMEDA)] (Halbach *et al.*, 2012). A reverse effect with a shortening of the Zn—O bonds *trans* to nitrogen was detected for [Zn(acac)$_2$(2,2′-bipyridine)] and [Zn(acac)$_2$(1,10-phenanthroline)] (Brahma *et al.*, 2008).

**Table 4**
Hydrogen-bond geometry (Å, °) for **2**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H2···O1$^{i}$ | 0.96 | 2.62 | 3.5269 (18) | 157 |

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

Each of the complexes **1**–**3** exhibits nearly planar six-membered acac-*M* chelate rings. The maximum deviation from planarity, as indicated by the dihedral angle between the M/O1/O2 (M/O3/O4) plane of the chelate ring and the best plane through O1/C2/C3/C4/O2 (O3/C7/C8/C9/O4), is 6.2 (1)° in the case of the zinc complex **3**. *PLATON* (Spek, 2009) was used to calculate the dihedral angles. The five-membered *M*-TMEDA ring adopts a twist conformation with approximate $C_2$ symmetry. As a result of the centrosymmetric crystal structure, both types of the enantiomeric chelate rings with λ and δ conformations are present.

The *MO*$_4$N$_2$ coordination polyhedra in compounds **1**–**3** deviate moderately from a regular octahedron. The O—*M*—O angles are in the range 171.7 (1)° (complex **1**) to 175.2 (1)° (complex **3**) and the N—*M*—O angles vary from 161.3 (1)° (complex **1**) to 170.9 (1)° (complex **2**). The smallest acac bite angle is observed in compound **1** [83.6 (1)°], the largest is found in compound **3** [88.0 (1)°]. In the case of the TMEDA ligands, the bite angles are marginally smaller with a range between 77.3 (1)° (compound **1**) and 80.3 (1)° (compound **3**). Overall, the distortion of the *MO*$_4$N$_2$ octahedra in compounds **1**–**3** is very similar to that observed in the analogous V, Ni and Co complexes [*M*(acac)$_2$(TMEDA)].

## 3. Supramolecular features

The packing of the [*M*(acac)$_2$(TMEDA)] units is dominated by van der Waals interactions. The mutual arrangement of the complex units **1**–**3** is similar but not identical (Figs. 4–6). In the case of the iron compound **2** there is also a contribution from weak C—H···O hydrogen bridges (Table 4). As a result, the complexes are associated by $R_2^2(8)$ type motifs, forming centrosymmetric dimers (Fig. 5).

## 4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.40, February 2019 update; Groom *et al.*, 2016) for complexes with a composition [*M*(acac)$_2$(TMEDA)] analogous to **1**–**3** revealed the crystal structures for the *M* = V, Ni, Co and Ru derivatives (Ma *et al.*, 1999; Pasko *et al.*, 2004; Trimmel *et al.*,

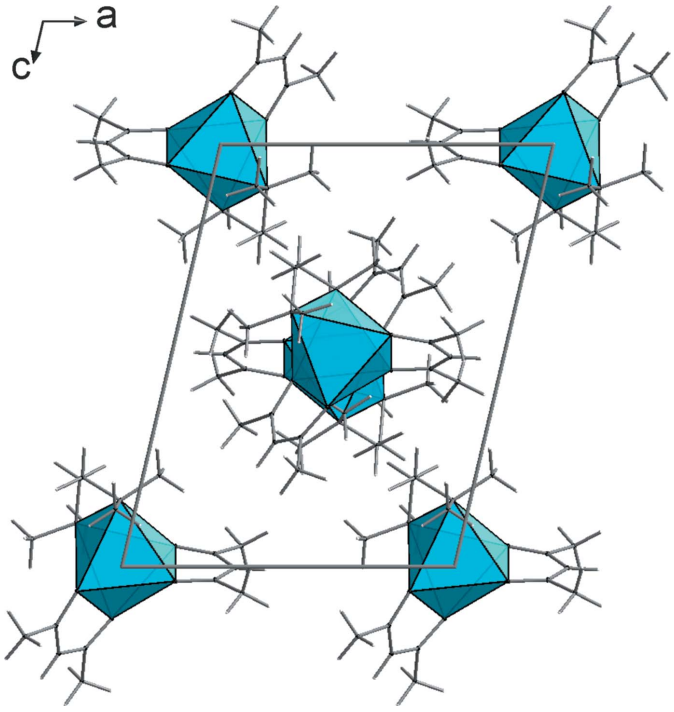



**Figure 4**
Crystal structure of compound **1**, viewed along the *b* axis.

2002; Zeller *et al.*, 2004; Halbach *et al.*, 2012). However, none of these complexes is isotypic with the three title compounds. In the case of the related hfa derivatives, complexes of the type $[M(\mathrm{hfa})_2(\mathrm{TMEDA})]$ (hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) with *M* = Mg, Mn, Fe, Co, Cu and Zn have been reported.

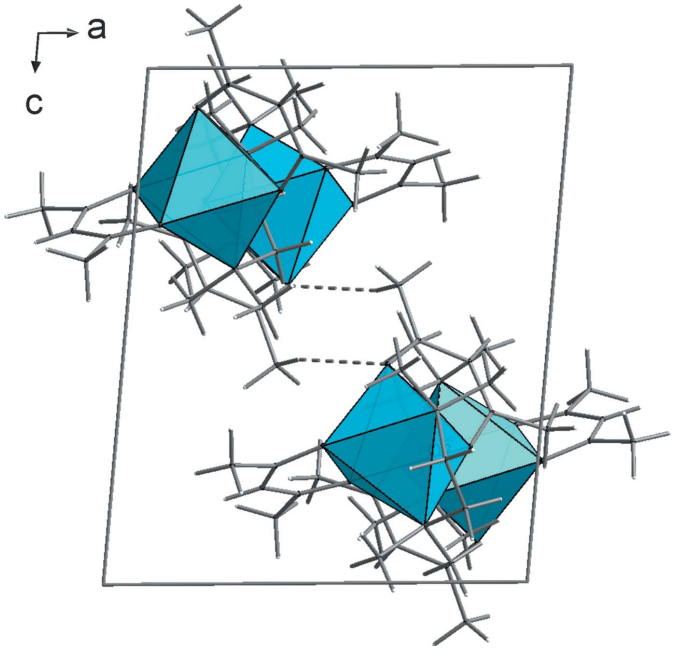



**Figure 5**
Crystal structure of compound **2**, viewed along the *b* axis. The intermolecular C—H···O hydrogen bonds are shown as dashed lines.

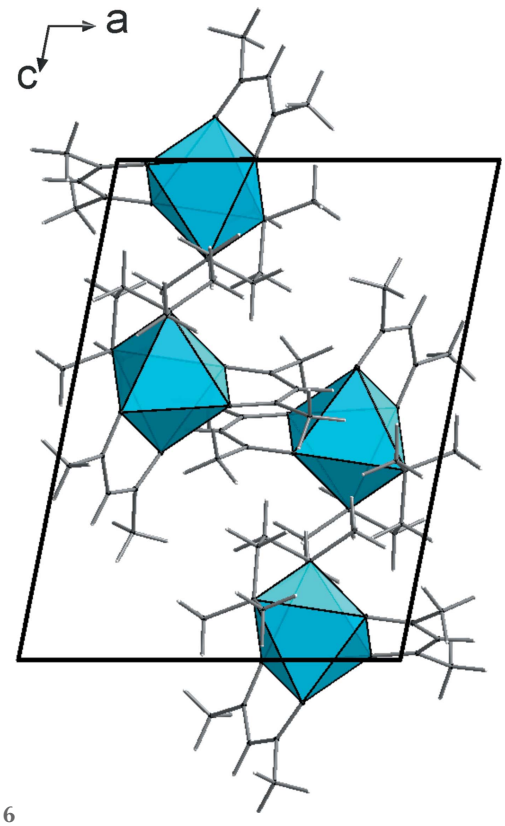



**Figure 6**
Crystal structure of compound **3**, viewed along the *b* axis.

## 5. Synthesis and crystallization

TMEDA (7.5 ml, 5.8 g, 50 mmol) was added to a suspension of $[M(\mathrm{acac})_2(\mathrm{H_2O})_2]$ (25 mmol, *M* = Mn: 9.71 g, Fe: 9.73 g, Zn: 9.97 g) in toluene (30 ml). The suspension was stirred at 323 K for 2 h. After removal of the solvent under reduced pressure, *n*-hexane (25 ml) was added and insoluble parts were filtered off. The filtrates were kept at 248 K to obtain the products as yellow (**1**), red–brown (**2**) and colourless (**3**) crystalline solids in yields around 90%.

**Characterization**

$[\mathrm{Mn(acac)_2TMEDA}]$ (**1**)

$C_{16}H_{30}MnN_2O_4$ calculated C 52.03, H 8.19, N 7.59%, found: C 51.71, H 8.13, N 7.14%; IR (ATR): $\nu$ = 3067 *w*, 2993 *w*, 2970 *w*, 2917 *w*, 2986 *w*, 2860 *w*, 2828 *w*, 2788 *w*, 2772 *w*, 1595 *m*, 1512 *s*, 1468 *m*, 1449 *m*, 1412 *s*, 1391 *m*, 1353 *m*, 1288 *m*, 1251 *m*, 1190 *w*, 1159 *w*, 1124 *w*, 1095 *w*, 1063 *w*, 1045 *m*, 1026 *w*, 1011 *m*, 950 *m*, 934 *w*, 913 *m*, 794 *m*, 771 *w*, 751 *m*, 650 *w*, 583 *w*, 526 *m*, 468 *w*, 448 *w*, 436 *w*, 400 *s*, 325 m, 212 s $cm^{-1}$.

M.p.: 362 K.

$[\mathrm{Fe(acac)_2TMEDA}]$ (**2**)

$C_{16}H_{30}FeN_2O_4$ calculated C 51.90, H 8.17, N 7.57%, found: C 51.75, H 8.08, N 7.23%; IR (ATR): $\nu$ = 3074 *w*, 3001 *w*, 2967 *w*, 2911 *w*, 2869 *w*, 2836 *w*, 2790 *w*, 1583 *m*, 1510 *s*, 1455 *m*, 1411 *s*, 1382 *m*, 1357 *w*, 1289 *m*, 1274 *w*, 1256 *m*, 1188 *w*, 1165 *w*, 1127 *w*, 1101 *w*, 1030 *w* 1012 *m*, 952 *m*, 917 *m*, 793 *m*, 762 *s*, 651 *w*, 583 *w*, 543 *m*, 475 *w*, 436 *w*, 404 *w*, 382 *s*, 296 *w*, 265 *m*, 227 *s* $cm^{-1}$.

M.p.: 361 K.

Table 5
Experimental details.

| | 1 | 2 | 3 |
|---|---|---|---|
| Crystal data | | | |
| Chemical formula | $[Mn(C_5H_7O_2)_2(C_6H_{16}N_2)]$ | $[Fe(C_5H_7O_2)_2(C_6H_{16}N_2)]$ | $[Zn(C_5H_7O_2)_2(C_6H_{16}N_2)]$ |
| $M_r$ | 369.36 | 370.27 | 379.79 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 213 | 213 | 200 |
| $a, b, c$ (Å) | 10.4234 (4), 14.3123 (5), 13.6047 (5) | 10.2021 (3), 15.4708 (4), 12.4881 (4) | 10.2335 (3), 14.2134 (6), 13.6738 (5) |
| $\beta$ (°) | 103.154 (3) | 95.382 (3) | 101.208 (3) |
| $V$ (Å$^3$) | 1976.33 (13) | 1962.37 (10) | 1950.96 (12) |
| $Z$ | 4 | 4 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.69 | 0.79 | 1.28 |
| Crystal size (mm) | 0.35 × 0.25 × 0.20 | 0.26 × 0.25 × 0.23 | 0.45 × 0.39 × 0.33 |
| Data collection | | | |
| Diffractometer | STOE IPDS 2 | STOE IPDS 2 | STOE IPDS 2T |
| Absorption correction | Numerical (*X-AREA*; Stoe & Cie, 2016) | Numerical (*X-AREA*; Stoe & Cie, 2016) | Numerical (*X-AREA*; Stoe & Cie, 2016) |
| $T_{min}$, $T_{max}$ | 0.798, 0.912 | 0.814, 0.894 | 0.627, 0.779 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12607, 4139, 3475 | 18586, 5276, 4425 | 22385, 4124, 3456 |
| $R_{int}$ | 0.030 | 0.037 | 0.047 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.634 | 0.688 | 0.633 |
| Refinement | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.034, 0.099, 1.06 | 0.031, 0.086, 1.04 | 0.027, 0.076, 1.07 |
| No. of reflections | 4139 | 5276 | 4124 |
| No. of parameters | 216 | 216 | 216 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.22, −0.24 | 0.32, −0.22 | 0.37, −0.26 |

Computer programs: *X-AREA* (Stoe & Cie, 2016), *SHELXT2014/7* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2019) and *OLEX2* (Dolomanov *et al.*, 2009).

[Zn(acac)$_2$TMEDA] (**3**)

$C_{16}H_{30}N_2O_4Zn$ calculated C 50.60, H 7.96, N 7.38%, found: C 50.33, H 8.13, N 7.23%; $^1$H-NMR ($CDCl_3$, 399.962 MHz) $\delta$ = 5.15 [*s*, 2H, C(O)C*H*C(O)], 2.49 (*s*, 4H, $Me_2$N-C$H_2$), 2.31 (*s*, 12H, $(CH_3)_2$N), 1.85 [*s*, 12H, $CH_3$C(O)]; $^{13}$C-NMR ($CDCl_3$,100.581 MHz) $\delta$ = 190.9 [*C*(O)], 98.4 [C(O)*C*HC(O)], 56.5 (N*C*H$_2$), 46.6 [(*C*H$_3$)$_2$N], 28.3 (C(O)*C*H$_3$) ppm; IR (ATR): $\nu$ = 3071 *w*, 3001 *w*, 2975 *w*, 2881 *w*, 2835 *w*, 2792 *w*, 1615 *m*, 1593 *m*, 1515 *s*, 1469 *m*, 1455 *m*, 1411 *m*, 1390 *s*, 1354 *m*, 1290 *m*, 1252 *m*, 1190 *w*, 1166 *w*, 1128 *w*, 1101 *w*, 1061 *w*, 1032 *m*, 1013 *s*, 953 *m*, 936 *w*, 918 *m*, 798 *m*, 770 *m*, 754 *m*, 649 *w*, 584 *w*, 543 *m*, 474 *w*, 440 *m*, 405 *s*, 382 *w*, 208 *s* cm$^{-1}$.

M.p.: 362 K.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. All hydrogen atoms were positioned geometrically and refined using a riding model with $U_{iso}$(H) = 1.2(CH and CH$_2$) or 1.5(CH$_3$) times $U_{eq}$(C). Reflections with error/e.s.d. > 8 were omitted. Error/e.s.d. = $(wD^2/<wD^2>)^{0.5}$ where $D = F_o^2 - F_c^2$.

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## References

Albrecht, R., Liebing, P., Morgenstern, U., Wagner, C. & Merzweiler, K. (2019). *Z. Naturforsch. Teil B*, **74**, 233–240.
Barreca, D., Carraro, G., Devi, A., Fois, E., Gasparotto, A., Seraglia, R., Maccato, C., Sada, C., Tabacchi, G., Tondello, E., Venzo, A. & Winter, M. (2012). *Dalton Trans.* **41**, 149–155.
Brahma, S., Sachin, H. P., Shivashankar, S. A., Narasimhamurthy, T. & Rathore, R. S. (2008). *Acta Cryst.* C**64**, m140–m143.
Brandenburg, K. (2019). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Dickman, M. H. (1998). *Acta Cryst.* C54 IUC9800048.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Gorkum, R. van, Buda, F., Kooijman, H., Spek, A. L., Bouwman, E. & Reedijk, J. (2005). *Eur. J. Inorg. Chem.* pp. 2255–2261.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Halbach, R. L., Nocton, G. & Andersen, R. A. (2012). *Dalton Trans.* **41**, 8809–8812.
Harbach, P., Lerner, H.-W. & Bolte, M. (2003). *Acta Cryst.* E**59**, m724–m725.
Kaschube, W., Pörschke, K. R. & Wilke, G. J. (1988). *J. Organomet. Chem.* **355**, 525–532.
Ma, Y. M., Reardon, D., Gambarotta, S., Yap, G., Zahalka, H. & Lemay, C. (1999). *Organometallics*, **18**, 2773–2781.

Malandrino, G., Toro, R. G., Catalano, M. R., Fragalà, M. E., Rossi, P. & Paoli, P. (2012). *Eur. J. Inorg. Chem.* pp.1021–1024.
Montgomery, H. & Lingafelter, E. C. (1968). *Acta Cryst.* B**24**, 1127–1128.
Nelkenbaum, E., Kapon, M. & Eisen, M. S. (2005). *Organometallics*, **24**, 2645–2659.
Ni, J., Yan, H., Wang, A., Yang, Y., Stern, C. L., Metz, A. W., Jin, S., Wang, L., Marks, T. J., Ireland, J. R. & Kannewurf, C. R. (2005). *J. Am. Chem. Soc.* **127**, 5613–5624.
Novitchi, G., Jiang, S., Shova, S., Rida, F., Hlavička, I., Orlita, M., Wernsdorfer, W., Hamze, R., Martins, C., Suaud, N., Guihéry, N., Barra, A.-L. & Train, C. (2017). *Inorg. Chem.* **56**, 14809–14822.
Pasko, S., Hubert-Pfalzgraf, L. G., Abrutis, A. & Vaissermann, J. (2004). *Polyhedron*, **23**, 735–741.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stephens, F. S. (1977). *Acta Cryst.* B**33**, 3492–3495.
Stoe & Cie (2016). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Trimmel, G., Lembacher, C., Kickelbick, G. & Schubert, U. (2002). *New J. Chem.* **26**, 759–765.
Tsodikov, M. V., Bukhtenko, O. V., Ellert, O. G., Petrunenko, I. A., Antsyshkina, A. S., Sadikov, G. G., Maksimov, Y. V., Titov, Y. V. & Novotortsev, V. M. (1995). *Russ. Chem. Bull.* **44**, 1396–1400.
Zeller, A., Herdtweck, E. & Strassner, Th. (2004). *Inorg. Chem. Commun.* **7**, 296–301.

# supporting information

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## Syntheses and crystal structures of three [*M*(acac)$_2$(TMEDA)] complexes (*M* = Mn, Fe and Zn)

**Jan Henrik Halz, Christian Heiser, Christoph Wagner and Kurt Merzweiler**

### Computing details

For all structures, data collection: *X-AREA* (Stoe & Cie, 2016); cell refinement: *X-AREA* (Stoe & Cie, 2016); data reduction: *X-AREA* (Stoe & Cie, 2016); program(s) used to solve structure: *SHELXT2014/7* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2019); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

**Bis(acetylacetonato-$\kappa^2O,O'$)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-$\kappa^2N,N'$)manganese(II) (1)**

*Crystal data*

$[Mn(C_5H_7O_2)_2(C_6H_{16}N_2)]$
$M_r$ = 369.36
Monoclinic, $P2_1/n$
$a$ = 10.4234 (4) Å
$b$ = 14.3123 (5) Å
$c$ = 13.6047 (5) Å
$\beta$ = 103.154 (3)°
$V$ = 1976.33 (13) Å$^3$
$Z$ = 4
$F(000)$ = 788
$D_x$ = 1.241 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 13227 reflections
$\theta$ = 1.4–27.2°
$\mu$ = 0.69 mm$^{-1}$
$T$ = 213 K
Block, clear yellow
0.35 × 0.25 × 0.20 mm

*Data collection*

STOE IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, Incoatec I$\mu$s
Plane graphite monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: numerical (X-AREA; Stoe & Cie, 2016)
$T_{min}$ = 0.798, $T_{max}$ = 0.912
12607 measured reflections
4139 independent reflections
3475 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030
$\theta_{max}$ = 26.8°, $\theta_{min}$ = 2.1°
$h$ = −13→13
$k$ = −17→18
$l$ = −17→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.099
$S$ = 1.06
4139 reflections
216 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.6571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Mn | 0.50579 (2) | 0.74721 (2) | 0.49407 (2) | 0.04120 (11) |
| O1 | 0.67069 (13) | 0.65614 (9) | 0.53426 (10) | 0.0602 (3) |
| O2 | 0.64605 (12) | 0.84003 (9) | 0.45153 (11) | 0.0554 (3) |
| O3 | 0.50538 (13) | 0.83274 (9) | 0.62280 (10) | 0.0546 (3) |
| O4 | 0.38216 (14) | 0.65820 (9) | 0.55845 (10) | 0.0565 (3) |
| N1 | 0.44810 (15) | 0.65991 (11) | 0.34289 (11) | 0.0523 (4) |
| N2 | 0.33093 (14) | 0.83481 (11) | 0.39666 (12) | 0.0533 (4) |
| C1 | 0.8801 (3) | 0.5868 (2) | 0.5617 (2) | 0.0943 (9) |
| H1 | 0.8477 | 0.5484 | 0.6086 | 0.141* |
| H3 | 0.9667 | 0.6089 | 0.5928 | 0.141* |
| H2 | 0.8838 | 0.5506 | 0.5029 | 0.141* |
| C2 | 0.7888 (2) | 0.66910 (16) | 0.53114 (14) | 0.0593 (5) |
| C3 | 0.8405 (2) | 0.75159 (16) | 0.50286 (17) | 0.0664 (6) |
| H4 | 0.9308 | 0.7532 | 0.5070 | 0.080* |
| C4 | 0.76938 (18) | 0.83223 (14) | 0.46880 (15) | 0.0568 (5) |
| C5 | 0.8448 (2) | 0.91826 (18) | 0.4505 (2) | 0.0885 (8) |
| H5 | 0.9136 | 0.9006 | 0.4178 | 0.133* |
| H6 | 0.8827 | 0.9477 | 0.5138 | 0.133* |
| H7 | 0.7860 | 0.9611 | 0.4082 | 0.133* |
| C6 | 0.4607 (2) | 0.89848 (16) | 0.77048 (18) | 0.0714 (6) |
| H8 | 0.5521 | 0.9144 | 0.7936 | 0.107* |
| H10 | 0.4263 | 0.8782 | 0.8267 | 0.107* |
| H9 | 0.4125 | 0.9522 | 0.7400 | 0.107* |
| C7 | 0.44674 (17) | 0.82045 (13) | 0.69347 (13) | 0.0498 (4) |
| C8 | 0.3712 (2) | 0.74328 (13) | 0.70557 (16) | 0.0568 (5) |
| H11 | 0.3367 | 0.7416 | 0.7629 | 0.068* |
| C9 | 0.34284 (19) | 0.66822 (13) | 0.63927 (15) | 0.0558 (4) |
| C10 | 0.2576 (3) | 0.59062 (18) | 0.6645 (2) | 0.0920 (9) |
| H12 | 0.2171 | 0.6107 | 0.7176 | 0.138* |
| H13 | 0.3109 | 0.5365 | 0.6861 | 0.138* |
| H14 | 0.1904 | 0.5754 | 0.6057 | 0.138* |
| C11 | 0.3189 (2) | 0.69516 (18) | 0.28808 (16) | 0.0693 (6) |
| H16 | 0.2506 | 0.6684 | 0.3173 | 0.083* |
| H15 | 0.3030 | 0.6753 | 0.2182 | 0.083* |
| C12 | 0.3114 (2) | 0.79961 (18) | 0.29216 (16) | 0.0703 (6) |
| H17 | 0.3781 | 0.8263 | 0.2612 | 0.084* |
| H18 | 0.2260 | 0.8199 | 0.2535 | 0.084* |
| C13 | 0.4397 (3) | 0.55956 (14) | 0.36410 (18) | 0.0728 (6) |
| H20 | 0.3743 | 0.5496 | 0.4026 | 0.109* |

| | | | | |
|---|---|---|---|---|
| H21 | 0.5236 | 0.5378 | 0.4018 | 0.109* |
| H19 | 0.4156 | 0.5258 | 0.3016 | 0.109* |
| C14 | 0.5481 (2) | 0.67378 (17) | 0.28339 (15) | 0.0647 (5) |
| H24 | 0.5227 | 0.6403 | 0.2208 | 0.097* |
| H22 | 0.6316 | 0.6509 | 0.3207 | 0.097* |
| H23 | 0.5553 | 0.7392 | 0.2698 | 0.097* |
| C15 | 0.21051 (19) | 0.82208 (18) | 0.43395 (18) | 0.0711 (6) |
| H25 | 0.1889 | 0.7568 | 0.4331 | 0.107* |
| H27 | 0.1393 | 0.8557 | 0.3914 | 0.107* |
| H26 | 0.2246 | 0.8454 | 0.5017 | 0.107* |
| C16 | 0.3638 (2) | 0.93462 (15) | 0.4003 (2) | 0.0784 (7) |
| H29 | 0.2945 | 0.9685 | 0.3560 | 0.118* |
| H28 | 0.4448 | 0.9435 | 0.3793 | 0.118* |
| H30 | 0.3736 | 0.9572 | 0.4680 | 0.118* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Mn | 0.03895 (15) | 0.04541 (18) | 0.03899 (15) | −0.00103 (10) | 0.00838 (10) | 0.00066 (10) |
| O1 | 0.0612 (8) | 0.0613 (8) | 0.0561 (8) | 0.0159 (6) | 0.0090 (6) | 0.0076 (6) |
| O2 | 0.0433 (6) | 0.0523 (7) | 0.0725 (9) | −0.0029 (5) | 0.0168 (6) | 0.0043 (6) |
| O3 | 0.0591 (7) | 0.0537 (7) | 0.0526 (7) | −0.0101 (6) | 0.0160 (6) | −0.0103 (6) |
| O4 | 0.0700 (8) | 0.0495 (7) | 0.0567 (8) | −0.0136 (6) | 0.0282 (6) | −0.0085 (6) |
| N1 | 0.0538 (8) | 0.0612 (9) | 0.0426 (8) | −0.0076 (7) | 0.0124 (6) | −0.0048 (7) |
| N2 | 0.0431 (7) | 0.0595 (9) | 0.0546 (9) | 0.0040 (7) | 0.0054 (6) | 0.0063 (7) |
| C1 | 0.0924 (18) | 0.108 (2) | 0.0744 (15) | 0.0575 (16) | 0.0027 (13) | −0.0049 (14) |
| C2 | 0.0561 (11) | 0.0758 (14) | 0.0411 (9) | 0.0216 (10) | 0.0009 (8) | −0.0109 (9) |
| C3 | 0.0392 (9) | 0.0933 (17) | 0.0658 (13) | 0.0089 (10) | 0.0100 (9) | −0.0196 (11) |
| C4 | 0.0454 (9) | 0.0699 (12) | 0.0589 (11) | −0.0094 (9) | 0.0197 (8) | −0.0190 (9) |
| C5 | 0.0657 (14) | 0.0870 (17) | 0.124 (2) | −0.0267 (13) | 0.0450 (15) | −0.0239 (16) |
| C6 | 0.0770 (14) | 0.0710 (14) | 0.0676 (13) | 0.0026 (11) | 0.0191 (11) | −0.0237 (11) |
| C7 | 0.0473 (9) | 0.0556 (10) | 0.0450 (9) | 0.0070 (8) | 0.0076 (7) | −0.0062 (8) |
| C8 | 0.0628 (12) | 0.0614 (12) | 0.0525 (10) | −0.0014 (9) | 0.0262 (9) | −0.0058 (8) |
| C9 | 0.0581 (10) | 0.0560 (11) | 0.0590 (11) | −0.0039 (9) | 0.0253 (9) | −0.0014 (9) |
| C10 | 0.110 (2) | 0.0822 (17) | 0.104 (2) | −0.0364 (15) | 0.0658 (17) | −0.0179 (15) |
| C11 | 0.0544 (11) | 0.0974 (17) | 0.0505 (11) | −0.0062 (11) | 0.0004 (9) | −0.0157 (11) |
| C12 | 0.0594 (12) | 0.0975 (17) | 0.0483 (11) | 0.0137 (11) | 0.0000 (9) | 0.0114 (11) |
| C13 | 0.1012 (17) | 0.0554 (12) | 0.0660 (13) | −0.0177 (11) | 0.0276 (12) | −0.0174 (10) |
| C14 | 0.0666 (12) | 0.0849 (15) | 0.0466 (10) | −0.0047 (11) | 0.0210 (9) | −0.0051 (10) |
| C15 | 0.0432 (10) | 0.0931 (16) | 0.0760 (14) | 0.0085 (10) | 0.0118 (9) | 0.0033 (12) |
| C16 | 0.0653 (13) | 0.0614 (13) | 0.1024 (19) | 0.0125 (10) | 0.0063 (12) | 0.0203 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Mn—O1 | 2.1271 (13) | C6—H10 | 0.9600 |
| Mn—O2 | 2.1500 (12) | C6—H9 | 0.9600 |
| Mn—O3 | 2.1375 (12) | C6—C7 | 1.515 (3) |
| Mn—O4 | 2.1365 (12) | C7—C8 | 1.388 (3) |

| | | | |
|---|---|---|---|
| Mn—N1 | 2.3643 (15) | C8—H11 | 0.9300 |
| Mn—N2 | 2.3560 (15) | C8—C9 | 1.391 (3) |
| O1—C2 | 1.255 (2) | C9—C10 | 1.510 (3) |
| O2—C4 | 1.258 (2) | C10—H12 | 0.9600 |
| O3—C7 | 1.263 (2) | C10—H13 | 0.9600 |
| O4—C9 | 1.266 (2) | C10—H14 | 0.9600 |
| N1—C11 | 1.472 (3) | C11—H16 | 0.9700 |
| N1—C13 | 1.472 (3) | C11—H15 | 0.9700 |
| N1—C14 | 1.472 (2) | C11—C12 | 1.499 (4) |
| N2—C12 | 1.478 (3) | C12—H17 | 0.9700 |
| N2—C15 | 1.468 (2) | C12—H18 | 0.9700 |
| N2—C16 | 1.467 (3) | C13—H20 | 0.9600 |
| C1—H1 | 0.9600 | C13—H21 | 0.9600 |
| C1—H3 | 0.9600 | C13—H19 | 0.9600 |
| C1—H2 | 0.9600 | C14—H24 | 0.9600 |
| C1—C2 | 1.512 (3) | C14—H22 | 0.9600 |
| C2—C3 | 1.388 (3) | C14—H23 | 0.9600 |
| C3—H4 | 0.9300 | C15—H25 | 0.9600 |
| C3—C4 | 1.393 (3) | C15—H27 | 0.9600 |
| C4—C5 | 1.512 (3) | C15—H26 | 0.9600 |
| C5—H5 | 0.9600 | C16—H29 | 0.9600 |
| C5—H6 | 0.9600 | C16—H28 | 0.9600 |
| C5—H7 | 0.9600 | C16—H30 | 0.9600 |
| C6—H8 | 0.9600 | | |

| | | | |
|---|---|---|---|
| O1—Mn—O2 | 83.61 (5) | C7—C6—H8 | 109.5 |
| O1—Mn—O3 | 107.00 (5) | C7—C6—H10 | 109.5 |
| O1—Mn—O4 | 93.25 (5) | C7—C6—H9 | 109.5 |
| O1—Mn—N1 | 86.01 (5) | O3—C7—C6 | 115.89 (17) |
| O1—Mn—N2 | 161.29 (6) | O3—C7—C8 | 125.92 (17) |
| O2—Mn—O3 | 89.71 (5) | C8—C7—C6 | 118.18 (17) |
| O2—Mn—O4 | 171.63 (5) | C7—C8—H11 | 117.2 |
| O2—Mn—N1 | 98.41 (5) | C7—C8—C9 | 125.50 (18) |
| O2—Mn—N2 | 90.36 (5) | C9—C8—H11 | 117.2 |
| O3—Mn—O4 | 83.78 (5) | O4—C9—C8 | 125.99 (17) |
| O3—Mn—N1 | 165.43 (5) | O4—C9—C10 | 115.94 (18) |
| O3—Mn—N2 | 90.61 (5) | C8—C9—C10 | 118.07 (18) |
| O4—Mn—N1 | 89.07 (5) | C9—C10—H12 | 109.5 |
| O4—Mn—N2 | 94.95 (6) | C9—C10—H13 | 109.5 |
| N1—Mn—N2 | 77.34 (6) | C9—C10—H14 | 109.5 |
| C2—O1—Mn | 129.95 (14) | H12—C10—H13 | 109.5 |
| C4—O2—Mn | 128.56 (13) | H12—C10—H14 | 109.5 |
| C7—O3—Mn | 129.44 (12) | H13—C10—H14 | 109.5 |
| C9—O4—Mn | 129.29 (12) | N1—C11—H16 | 109.2 |
| C11—N1—Mn | 106.37 (12) | N1—C11—H15 | 109.2 |
| C13—N1—Mn | 111.10 (12) | N1—C11—C12 | 111.88 (17) |
| C13—N1—C11 | 110.20 (18) | H16—C11—H15 | 107.9 |
| C13—N1—C14 | 108.71 (17) | C12—C11—H16 | 109.2 |

| | | | |
|---|---|---|---|
| C14—N1—Mn | 109.60 (12) | C12—C11—H15 | 109.2 |
| C14—N1—C11 | 110.86 (16) | N2—C12—C11 | 112.25 (17) |
| C12—N2—Mn | 106.22 (12) | N2—C12—H17 | 109.2 |
| C15—N2—Mn | 110.63 (12) | N2—C12—H18 | 109.2 |
| C15—N2—C12 | 110.40 (17) | C11—C12—H17 | 109.2 |
| C16—N2—Mn | 110.75 (12) | C11—C12—H18 | 109.2 |
| C16—N2—C12 | 110.14 (18) | H17—C12—H18 | 107.9 |
| C16—N2—C15 | 108.69 (17) | N1—C13—H20 | 109.5 |
| H1—C1—H3 | 109.5 | N1—C13—H21 | 109.5 |
| H1—C1—H2 | 109.5 | N1—C13—H19 | 109.5 |
| H3—C1—H2 | 109.5 | H20—C13—H21 | 109.5 |
| C2—C1—H1 | 109.5 | H20—C13—H19 | 109.5 |
| C2—C1—H3 | 109.5 | H21—C13—H19 | 109.5 |
| C2—C1—H2 | 109.5 | N1—C14—H24 | 109.5 |
| O1—C2—C1 | 115.9 (2) | N1—C14—H22 | 109.5 |
| O1—C2—C3 | 125.51 (18) | N1—C14—H23 | 109.5 |
| C3—C2—C1 | 118.6 (2) | H24—C14—H22 | 109.5 |
| C2—C3—H4 | 117.1 | H24—C14—H23 | 109.5 |
| C2—C3—C4 | 125.86 (18) | H22—C14—H23 | 109.5 |
| C4—C3—H4 | 117.1 | N2—C15—H25 | 109.5 |
| O2—C4—C3 | 125.44 (19) | N2—C15—H27 | 109.5 |
| O2—C4—C5 | 116.4 (2) | N2—C15—H26 | 109.5 |
| C3—C4—C5 | 118.17 (19) | H25—C15—H27 | 109.5 |
| C4—C5—H5 | 109.5 | H25—C15—H26 | 109.5 |
| C4—C5—H6 | 109.5 | H27—C15—H26 | 109.5 |
| C4—C5—H7 | 109.5 | N2—C16—H29 | 109.5 |
| H5—C5—H6 | 109.5 | N2—C16—H28 | 109.5 |
| H5—C5—H7 | 109.5 | N2—C16—H30 | 109.5 |
| H6—C5—H7 | 109.5 | H29—C16—H28 | 109.5 |
| H8—C6—H10 | 109.5 | H29—C16—H30 | 109.5 |
| H8—C6—H9 | 109.5 | H28—C16—H30 | 109.5 |
| H10—C6—H9 | 109.5 | | |

| | | | |
|---|---|---|---|
| Mn—O1—C2—C1 | −177.50 (14) | N1—C11—C12—N2 | −60.6 (2) |
| Mn—O1—C2—C3 | 2.8 (3) | C1—C2—C3—C4 | 177.1 (2) |
| Mn—O2—C4—C3 | 13.4 (3) | C2—C3—C4—O2 | −5.6 (3) |
| Mn—O2—C4—C5 | −166.67 (16) | C2—C3—C4—C5 | 174.5 (2) |
| Mn—O3—C7—C6 | −176.26 (13) | C6—C7—C8—C9 | 176.5 (2) |
| Mn—O3—C7—C8 | 3.2 (3) | C7—C8—C9—O4 | 0.7 (4) |
| Mn—O4—C9—C8 | 1.1 (3) | C7—C8—C9—C10 | −179.4 (2) |
| Mn—O4—C9—C10 | −178.82 (17) | C13—N1—C11—C12 | 162.74 (17) |
| Mn—N1—C11—C12 | 42.22 (19) | C14—N1—C11—C12 | −76.9 (2) |
| Mn—N2—C12—C11 | 42.41 (19) | C15—N2—C12—C11 | −77.6 (2) |
| O1—C2—C3—C4 | −3.2 (3) | C16—N2—C12—C11 | 162.39 (17) |
| O3—C7—C8—C9 | −3.0 (3) | | |

**Bis(acetylacetonato-$\kappa^2O,O'$)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-$\kappa^2N,N'$)iron(II) (2)**

*Crystal data*

$[Fe(C_5H_7O_2)_2(C_6H_{16}N_2)]$
$M_r = 370.27$
Monoclinic, $P2_1/n$
$a = 10.2021$ (3) Å
$b = 15.4708$ (4) Å
$c = 12.4881$ (4) Å
$\beta = 95.382$ (3)°
$V = 1962.37$ (10) Å$^3$
$Z = 4$
$F(000) = 792$
$D_x = 1.253$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 16780 reflections
$\theta = 1.6$–29.6°
$\mu = 0.79$ mm$^{-1}$
$T = 213$ K
Block, clear reddish brown
0.26 × 0.25 × 0.23 mm

*Data collection*

STOE IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, Incoatec I$\mu$s
Plane graphite monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: numerical (X-AREA; Stoe & Cie, 2016)
$T_{min} = 0.814$, $T_{max} = 0.894$
18586 measured reflections
5276 independent reflections
4425 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 29.3°$, $\theta_{min} = 2.1°$
$h = -13\rightarrow13$
$k = -21\rightarrow20$
$l = -17\rightarrow17$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.086$
$S = 1.04$
5276 reflections
216 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.3681P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.22$ e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.63613 (15) | 0.53037 (11) | 0.42322 (12) | 0.0444 (3) |
| H2 | 0.5847 | 0.4797 | 0.4338 | 0.067* |
| H3 | 0.7061 | 0.5160 | 0.3800 | 0.067* |
| H1 | 0.5810 | 0.5739 | 0.3874 | 0.067* |
| C2 | 0.69359 (13) | 0.56425 (9) | 0.53071 (11) | 0.0352 (3) |
| C3 | 0.81769 (14) | 0.53357 (9) | 0.57243 (12) | 0.0396 (3) |
| H4 | 0.8603 | 0.4948 | 0.5305 | 0.047* |
| C4 | 0.88149 (13) | 0.55660 (9) | 0.67116 (12) | 0.0388 (3) |
| C5 | 1.01582 (16) | 0.51923 (13) | 0.70525 (16) | 0.0584 (4) |
| H7 | 1.0343 | 0.4733 | 0.6572 | 0.088* |

| | | | | |
|---|---|---|---|---|
| H5 | 1.0172 | 0.4970 | 0.7771 | 0.088* |
| H6 | 1.0813 | 0.5636 | 0.7031 | 0.088* |
| C6 | 0.39240 (17) | 0.48770 (10) | 0.87153 (14) | 0.0496 (4) |
| H10 | 0.3000 | 0.4817 | 0.8499 | 0.074* |
| H9 | 0.4064 | 0.4888 | 0.9486 | 0.074* |
| H8 | 0.4391 | 0.4397 | 0.8446 | 0.074* |
| C7 | 0.44227 (13) | 0.57093 (9) | 0.82668 (11) | 0.0359 (3) |
| C8 | 0.35444 (13) | 0.64029 (10) | 0.81410 (12) | 0.0379 (3) |
| H11 | 0.2707 | 0.6321 | 0.8359 | 0.046* |
| C9 | 0.38200 (13) | 0.72026 (9) | 0.77178 (11) | 0.0350 (3) |
| C10 | 0.27918 (16) | 0.79023 (12) | 0.77050 (16) | 0.0542 (4) |
| H14 | 0.2694 | 0.8171 | 0.7009 | 0.081* |
| H13 | 0.3059 | 0.8328 | 0.8241 | 0.081* |
| H12 | 0.1967 | 0.7654 | 0.7857 | 0.081* |
| C11 | 0.78186 (19) | 0.85071 (11) | 0.76164 (14) | 0.0537 (4) |
| H16 | 0.7020 | 0.8793 | 0.7792 | 0.064* |
| H15 | 0.8440 | 0.8949 | 0.7446 | 0.064* |
| C12 | 0.83901 (17) | 0.80004 (13) | 0.85721 (14) | 0.0545 (4) |
| H17 | 0.9192 | 0.7718 | 0.8398 | 0.065* |
| H18 | 0.8617 | 0.8393 | 0.9167 | 0.065* |
| C13 | 0.6596 (2) | 0.83936 (13) | 0.58754 (16) | 0.0593 (4) |
| H19 | 0.6381 | 0.8022 | 0.5269 | 0.089* |
| H21 | 0.7000 | 0.8912 | 0.5641 | 0.089* |
| H20 | 0.5807 | 0.8539 | 0.6198 | 0.089* |
| C14 | 0.87086 (16) | 0.77473 (12) | 0.61406 (14) | 0.0519 (4) |
| H24 | 0.9042 | 0.8268 | 0.5847 | 0.078* |
| H22 | 0.8499 | 0.7338 | 0.5572 | 0.078* |
| H23 | 0.9363 | 0.7506 | 0.6658 | 0.078* |
| C15 | 0.64471 (18) | 0.77489 (13) | 0.94987 (14) | 0.0549 (4) |
| H26 | 0.5825 | 0.7319 | 0.9677 | 0.082* |
| H25 | 0.6001 | 0.8188 | 0.9060 | 0.082* |
| H27 | 0.6853 | 0.8005 | 1.0147 | 0.082* |
| C16 | 0.8174 (2) | 0.67090 (14) | 0.96194 (14) | 0.0619 (5) |
| H29 | 0.8834 | 0.6428 | 0.9244 | 0.093* |
| H28 | 0.7566 | 0.6286 | 0.9840 | 0.093* |
| H30 | 0.8587 | 0.7000 | 1.0242 | 0.093* |
| Fe | 0.65967 (2) | 0.67126 (2) | 0.73081 (2) | 0.03242 (7) |
| N1 | 0.75139 (12) | 0.79468 (8) | 0.66685 (10) | 0.0407 (3) |
| N2 | 0.74634 (12) | 0.73421 (9) | 0.89046 (10) | 0.0418 (3) |
| O1 | 0.62568 (9) | 0.61851 (7) | 0.57684 (8) | 0.0395 (2) |
| O2 | 0.83743 (9) | 0.60880 (7) | 0.73746 (9) | 0.0426 (2) |
| O3 | 0.55981 (10) | 0.57212 (6) | 0.80388 (9) | 0.0414 (2) |
| O4 | 0.48936 (9) | 0.74134 (6) | 0.73429 (8) | 0.0384 (2) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0435 (7) | 0.0512 (8) | 0.0393 (7) | −0.0086 (6) | 0.0082 (6) | −0.0108 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0360 (6) | 0.0341 (6) | 0.0368 (7) | −0.0081 (5) | 0.0096 (5) | −0.0039 (5) |
| C3 | 0.0380 (7) | 0.0368 (7) | 0.0453 (8) | 0.0022 (5) | 0.0111 (6) | −0.0064 (6) |
| C4 | 0.0301 (6) | 0.0407 (7) | 0.0465 (8) | 0.0000 (5) | 0.0089 (5) | 0.0000 (6) |
| C5 | 0.0374 (8) | 0.0703 (12) | 0.0670 (11) | 0.0127 (8) | 0.0019 (7) | −0.0056 (9) |
| C6 | 0.0539 (9) | 0.0434 (8) | 0.0515 (9) | −0.0121 (7) | 0.0050 (7) | 0.0076 (7) |
| C7 | 0.0380 (6) | 0.0369 (7) | 0.0328 (6) | −0.0079 (5) | 0.0028 (5) | −0.0029 (5) |
| C8 | 0.0303 (6) | 0.0435 (7) | 0.0413 (7) | −0.0049 (5) | 0.0102 (5) | −0.0045 (6) |
| C9 | 0.0315 (6) | 0.0393 (7) | 0.0349 (6) | 0.0017 (5) | 0.0056 (5) | −0.0047 (5) |
| C10 | 0.0439 (8) | 0.0539 (9) | 0.0670 (11) | 0.0149 (7) | 0.0163 (7) | 0.0022 (8) |
| C11 | 0.0674 (11) | 0.0428 (8) | 0.0540 (10) | −0.0207 (8) | 0.0222 (8) | −0.0125 (7) |
| C12 | 0.0508 (9) | 0.0685 (11) | 0.0451 (9) | −0.0275 (8) | 0.0092 (7) | −0.0158 (8) |
| C13 | 0.0626 (11) | 0.0614 (11) | 0.0559 (10) | −0.0011 (8) | 0.0154 (8) | 0.0167 (8) |
| C14 | 0.0496 (8) | 0.0561 (9) | 0.0537 (9) | −0.0149 (7) | 0.0247 (7) | −0.0073 (7) |
| C15 | 0.0550 (9) | 0.0690 (11) | 0.0429 (8) | −0.0094 (8) | 0.0167 (7) | −0.0164 (8) |
| C16 | 0.0650 (11) | 0.0792 (13) | 0.0401 (9) | 0.0011 (9) | −0.0027 (8) | −0.0002 (8) |
| Fe | 0.02688 (10) | 0.03490 (11) | 0.03626 (11) | −0.00268 (7) | 0.00714 (7) | −0.00567 (7) |
| N1 | 0.0432 (6) | 0.0415 (6) | 0.0395 (6) | −0.0086 (5) | 0.0147 (5) | −0.0039 (5) |
| N2 | 0.0395 (6) | 0.0513 (7) | 0.0354 (6) | −0.0101 (5) | 0.0077 (5) | −0.0055 (5) |
| O1 | 0.0329 (5) | 0.0440 (5) | 0.0416 (5) | 0.0005 (4) | 0.0028 (4) | −0.0112 (4) |
| O2 | 0.0313 (5) | 0.0535 (6) | 0.0429 (5) | 0.0021 (4) | 0.0031 (4) | −0.0100 (5) |
| O3 | 0.0352 (5) | 0.0352 (5) | 0.0543 (6) | −0.0009 (4) | 0.0075 (4) | 0.0014 (4) |
| O4 | 0.0349 (5) | 0.0348 (5) | 0.0471 (5) | 0.0018 (4) | 0.0124 (4) | 0.0023 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—H2 | 0.9600 | C11—C12 | 1.499 (3) |
| C1—H3 | 0.9600 | C11—N1 | 1.477 (2) |
| C1—H1 | 0.9600 | C12—H17 | 0.9700 |
| C1—C2 | 1.5076 (19) | C12—H18 | 0.9700 |
| C2—C3 | 1.406 (2) | C12—N2 | 1.475 (2) |
| C2—O1 | 1.2615 (16) | C13—H19 | 0.9600 |
| C3—H4 | 0.9300 | C13—H21 | 0.9600 |
| C3—C4 | 1.386 (2) | C13—H20 | 0.9600 |
| C4—C5 | 1.511 (2) | C13—N1 | 1.471 (2) |
| C4—O2 | 1.2687 (17) | C14—H24 | 0.9600 |
| C5—H7 | 0.9600 | C14—H22 | 0.9600 |
| C5—H5 | 0.9600 | C14—H23 | 0.9600 |
| C5—H6 | 0.9600 | C14—N1 | 1.4718 (19) |
| C6—H10 | 0.9600 | C15—H26 | 0.9600 |
| C6—H9 | 0.9600 | C15—H25 | 0.9600 |
| C6—H8 | 0.9600 | C15—H27 | 0.9600 |
| C6—C7 | 1.511 (2) | C15—N2 | 1.472 (2) |
| C7—C8 | 1.397 (2) | C16—H29 | 0.9600 |
| C7—O3 | 1.2583 (17) | C16—H28 | 0.9600 |
| C8—H11 | 0.9300 | C16—H30 | 0.9600 |
| C8—C9 | 1.385 (2) | C16—N2 | 1.470 (2) |
| C9—C10 | 1.506 (2) | Fe—O1 | 2.0876 (10) |
| C9—O4 | 1.2734 (16) | Fe—O2 | 2.0497 (10) |

| | | | |
|---|---|---|---|
| C10—H14 | 0.9600 | Fe—O3 | 2.0970 (10) |
| C10—H13 | 0.9600 | Fe—O4 | 2.0520 (9) |
| C10—H12 | 0.9600 | Fe—N1 | 2.3021 (12) |
| C11—H16 | 0.9700 | Fe—N2 | 2.3184 (12) |
| C11—H15 | 0.9700 | | |

| | | | |
|---|---|---|---|
| H2—C1—H3 | 109.5 | H19—C13—H20 | 109.5 |
| H2—C1—H1 | 109.5 | H21—C13—H20 | 109.5 |
| H3—C1—H1 | 109.5 | N1—C13—H19 | 109.5 |
| C2—C1—H2 | 109.5 | N1—C13—H21 | 109.5 |
| C2—C1—H3 | 109.5 | N1—C13—H20 | 109.5 |
| C2—C1—H1 | 109.5 | H24—C14—H22 | 109.5 |
| C3—C2—C1 | 118.30 (12) | H24—C14—H23 | 109.5 |
| O1—C2—C1 | 116.98 (13) | H22—C14—H23 | 109.5 |
| O1—C2—C3 | 124.72 (13) | N1—C14—H24 | 109.5 |
| C2—C3—H4 | 117.5 | N1—C14—H22 | 109.5 |
| C4—C3—C2 | 125.07 (13) | N1—C14—H23 | 109.5 |
| C4—C3—H4 | 117.5 | H26—C15—H25 | 109.5 |
| C3—C4—C5 | 119.35 (14) | H26—C15—H27 | 109.5 |
| O2—C4—C3 | 125.36 (13) | H25—C15—H27 | 109.5 |
| O2—C4—C5 | 115.28 (14) | N2—C15—H26 | 109.5 |
| C4—C5—H7 | 109.5 | N2—C15—H25 | 109.5 |
| C4—C5—H5 | 109.5 | N2—C15—H27 | 109.5 |
| C4—C5—H6 | 109.5 | H29—C16—H28 | 109.5 |
| H7—C5—H5 | 109.5 | H29—C16—H30 | 109.5 |
| H7—C5—H6 | 109.5 | H28—C16—H30 | 109.5 |
| H5—C5—H6 | 109.5 | N2—C16—H29 | 109.5 |
| H10—C6—H9 | 109.5 | N2—C16—H28 | 109.5 |
| H10—C6—H8 | 109.5 | N2—C16—H30 | 109.5 |
| H9—C6—H8 | 109.5 | O1—Fe—O2 | 85.58 (4) |
| C7—C6—H10 | 109.5 | O1—Fe—O3 | 93.98 (4) |
| C7—C6—H9 | 109.5 | O1—Fe—O4 | 99.11 (4) |
| C7—C6—H8 | 109.5 | O1—Fe—N1 | 92.44 (4) |
| C8—C7—C6 | 117.47 (13) | O1—Fe—N2 | 166.73 (4) |
| O3—C7—C6 | 117.22 (13) | O2—Fe—O3 | 95.84 (4) |
| O3—C7—C8 | 125.31 (13) | O2—Fe—O4 | 174.85 (4) |
| C7—C8—H11 | 117.3 | O2—Fe—N1 | 91.04 (5) |
| C9—C8—C7 | 125.32 (12) | O2—Fe—N2 | 84.18 (4) |
| C9—C8—H11 | 117.3 | O3—Fe—O4 | 86.00 (4) |
| C8—C9—C10 | 118.69 (13) | O3—Fe—N1 | 170.93 (4) |
| O4—C9—C8 | 125.57 (12) | O3—Fe—N2 | 95.43 (4) |
| O4—C9—C10 | 115.74 (13) | O4—Fe—N1 | 86.66 (4) |
| C9—C10—H14 | 109.5 | O4—Fe—N2 | 90.87 (4) |
| C9—C10—H13 | 109.5 | N1—Fe—N2 | 79.35 (4) |
| C9—C10—H12 | 109.5 | C11—N1—Fe | 105.70 (9) |
| H14—C10—H13 | 109.5 | C13—N1—C11 | 109.69 (14) |
| H14—C10—H12 | 109.5 | C13—N1—C14 | 107.39 (13) |
| H13—C10—H12 | 109.5 | C13—N1—Fe | 111.69 (10) |

| | | | |
|---|---|---|---|
| H16—C11—H15 | 108.0 | C14—N1—C11 | 111.18 (13) |
| C12—C11—H16 | 109.3 | C14—N1—Fe | 111.24 (10) |
| C12—C11—H15 | 109.3 | C12—N2—Fe | 104.52 (9) |
| N1—C11—H16 | 109.3 | C15—N2—C12 | 110.31 (14) |
| N1—C11—H15 | 109.3 | C15—N2—Fe | 112.54 (10) |
| N1—C11—C12 | 111.60 (14) | C16—N2—C12 | 109.77 (14) |
| C11—C12—H17 | 109.2 | C16—N2—C15 | 108.03 (14) |
| C11—C12—H18 | 109.2 | C16—N2—Fe | 111.65 (10) |
| H17—C12—H18 | 107.9 | C2—O1—Fe | 129.04 (9) |
| N2—C12—C11 | 111.91 (13) | C4—O2—Fe | 129.79 (9) |
| N2—C12—H17 | 109.2 | C7—O3—Fe | 128.42 (10) |
| N2—C12—H18 | 109.2 | C9—O4—Fe | 129.18 (9) |
| H19—C13—H21 | 109.5 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H2···O1$^{i}$ | 0.96 | 2.62 | 3.5269 (18) | 157 |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

## Bis(acetylacetonato-$\kappa^2O,O'$)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-$\kappa^2N,N'$)zinc(II) (3)

*Crystal data*

$[Zn(C_5H_7O_2)_2(C_6H_{16}N_2)]$
$M_r$ = 379.79
Monoclinic, $P2_1/n$
$a$ = 10.2335 (3) Å
$b$ = 14.2134 (6) Å
$c$ = 13.6738 (5) Å
$\beta$ = 101.208 (3)°
$V$ = 1950.96 (12) Å$^3$
$Z$ = 4
$F(000)$ = 808
$D_x$ = 1.293 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 19126 reflections
$\theta$ = 2.1–27.2°
$\mu$ = 1.28 mm$^{-1}$
$T$ = 200 K
Block, clear colourless
0.45 × 0.39 × 0.33 mm

*Data collection*

STOE IPDS 2T diffractometer
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method, $\omega$ scans
Absorption correction: numerical (X-AREA; Stoe & Cie, 2016)
$T_{min}$ = 0.627, $T_{max}$ = 0.779
22385 measured reflections
4124 independent reflections
3456 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.047
$\theta_{max}$ = 26.7°, $\theta_{min}$ = 2.1°
$h$ = −12→12
$k$ = −17→16
$l$ = −17→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.076
$S$ = 1.07
4124 reflections
216 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn | 0.74026 (2) | 0.26429 (2) | 0.54676 (2) | 0.03991 (8) |
| O1 | 0.73445 (12) | 0.33774 (8) | 0.41466 (9) | 0.0534 (3) |
| O2 | 0.85986 (11) | 0.16705 (8) | 0.49492 (8) | 0.0507 (3) |
| O3 | 0.57869 (11) | 0.17554 (8) | 0.50853 (9) | 0.0529 (3) |
| O4 | 0.61242 (9) | 0.36299 (8) | 0.58630 (8) | 0.0441 (2) |
| N1 | 0.91461 (12) | 0.35505 (11) | 0.62041 (10) | 0.0499 (3) |
| N2 | 0.78674 (12) | 0.19573 (11) | 0.69813 (10) | 0.0459 (3) |
| C1 | 0.76595 (19) | 0.38103 (13) | 0.25509 (13) | 0.0575 (4) |
| H1 | 0.6725 | 0.4006 | 0.2373 | 0.086* |
| H2 | 0.7922 | 0.3504 | 0.1977 | 0.086* |
| H3 | 0.8222 | 0.4363 | 0.2743 | 0.086* |
| C2 | 0.78276 (15) | 0.31277 (12) | 0.34146 (11) | 0.0450 (4) |
| C3 | 0.85137 (17) | 0.22957 (12) | 0.33344 (13) | 0.0492 (4) |
| H4 | 0.8764 | 0.2169 | 0.2714 | 0.059* |
| C4 | 0.88628 (15) | 0.16331 (12) | 0.40893 (12) | 0.0462 (4) |
| C5 | 0.9672 (2) | 0.07864 (15) | 0.38836 (14) | 0.0672 (5) |
| H5 | 1.0493 | 0.0752 | 0.4389 | 0.101* |
| H6 | 0.9896 | 0.0849 | 0.3222 | 0.101* |
| H7 | 0.9149 | 0.0212 | 0.3907 | 0.101* |
| C6 | 0.3632 (2) | 0.11210 (15) | 0.48710 (15) | 0.0691 (5) |
| H8 | 0.3797 | 0.0646 | 0.5401 | 0.104* |
| H9 | 0.3758 | 0.0838 | 0.4242 | 0.104* |
| H10 | 0.2717 | 0.1354 | 0.4796 | 0.104* |
| C7 | 0.45930 (16) | 0.19273 (13) | 0.51387 (11) | 0.0476 (4) |
| C8 | 0.41127 (15) | 0.27812 (12) | 0.54200 (12) | 0.0475 (4) |
| H11 | 0.3180 | 0.2826 | 0.5391 | 0.057* |
| C9 | 0.48712 (14) | 0.35764 (11) | 0.57395 (11) | 0.0412 (3) |
| C10 | 0.41684 (16) | 0.44556 (13) | 0.59729 (13) | 0.0554 (4) |
| H12 | 0.3393 | 0.4283 | 0.6257 | 0.083* |
| H13 | 0.3875 | 0.4817 | 0.5359 | 0.083* |
| H14 | 0.4780 | 0.4838 | 0.6454 | 0.083* |
| C11 | 0.93211 (19) | 0.33443 (17) | 0.72727 (14) | 0.0676 (5) |
| H15 | 0.8644 | 0.3692 | 0.7556 | 0.081* |
| H16 | 1.0212 | 0.3563 | 0.7615 | 0.081* |
| C12 | 0.91917 (19) | 0.23151 (16) | 0.74583 (15) | 0.0651 (5) |
| H17 | 0.9887 | 0.1969 | 0.7194 | 0.078* |
| H18 | 0.9335 | 0.2200 | 0.8185 | 0.078* |
| C13 | 0.88618 (18) | 0.45547 (14) | 0.60157 (16) | 0.0671 (5) |
| H19 | 0.9629 | 0.4929 | 0.6341 | 0.101* |

| | | | | |
|---|---|---|---|---|
| H20 | 0.8076 | 0.4732 | 0.6285 | 0.101* |
| H21 | 0.8691 | 0.4673 | 0.5296 | 0.101* |
| C14 | 1.03600 (16) | 0.33196 (16) | 0.58256 (16) | 0.0651 (5) |
| H22 | 1.0212 | 0.3449 | 0.5108 | 0.098* |
| H23 | 1.0573 | 0.2652 | 0.5944 | 0.098* |
| H24 | 1.1102 | 0.3704 | 0.6172 | 0.098* |
| C15 | 0.68709 (18) | 0.21961 (14) | 0.75840 (13) | 0.0560 (4) |
| H25 | 0.6835 | 0.2881 | 0.7660 | 0.084* |
| H26 | 0.7118 | 0.1902 | 0.8243 | 0.084* |
| H27 | 0.5995 | 0.1964 | 0.7251 | 0.084* |
| C16 | 0.7902 (2) | 0.09286 (14) | 0.68935 (15) | 0.0680 (5) |
| H28 | 0.7024 | 0.0700 | 0.6562 | 0.102* |
| H29 | 0.8137 | 0.0649 | 0.7560 | 0.102* |
| H30 | 0.8568 | 0.0750 | 0.6500 | 0.102* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn | 0.03590 (11) | 0.04475 (13) | 0.04087 (12) | 0.00666 (7) | 0.01186 (8) | −0.00208 (7) |
| O1 | 0.0628 (7) | 0.0534 (7) | 0.0470 (6) | 0.0178 (6) | 0.0187 (5) | 0.0051 (5) |
| O2 | 0.0555 (6) | 0.0545 (7) | 0.0465 (6) | 0.0158 (5) | 0.0204 (5) | 0.0024 (5) |
| O3 | 0.0488 (6) | 0.0496 (7) | 0.0592 (7) | −0.0007 (5) | 0.0078 (5) | −0.0096 (5) |
| O4 | 0.0335 (5) | 0.0470 (6) | 0.0538 (6) | 0.0028 (4) | 0.0136 (4) | −0.0040 (5) |
| N1 | 0.0353 (6) | 0.0602 (9) | 0.0557 (8) | −0.0041 (6) | 0.0125 (6) | −0.0053 (7) |
| N2 | 0.0431 (7) | 0.0537 (8) | 0.0422 (7) | 0.0079 (6) | 0.0114 (5) | 0.0024 (6) |
| C1 | 0.0653 (11) | 0.0582 (11) | 0.0492 (10) | −0.0021 (9) | 0.0114 (8) | 0.0046 (8) |
| C2 | 0.0406 (8) | 0.0525 (10) | 0.0417 (8) | −0.0032 (7) | 0.0077 (6) | −0.0012 (7) |
| C3 | 0.0529 (9) | 0.0559 (10) | 0.0417 (9) | 0.0035 (7) | 0.0163 (7) | −0.0050 (7) |
| C4 | 0.0444 (8) | 0.0481 (9) | 0.0485 (9) | 0.0042 (7) | 0.0149 (7) | −0.0079 (7) |
| C5 | 0.0817 (13) | 0.0620 (12) | 0.0632 (11) | 0.0230 (10) | 0.0271 (10) | −0.0048 (9) |
| C6 | 0.0680 (12) | 0.0741 (14) | 0.0632 (12) | −0.0250 (10) | 0.0074 (9) | −0.0086 (10) |
| C7 | 0.0474 (8) | 0.0576 (10) | 0.0356 (8) | −0.0083 (8) | 0.0028 (6) | 0.0009 (7) |
| C8 | 0.0323 (7) | 0.0653 (11) | 0.0451 (9) | −0.0004 (7) | 0.0081 (6) | 0.0028 (7) |
| C9 | 0.0368 (7) | 0.0515 (9) | 0.0370 (8) | 0.0066 (6) | 0.0113 (6) | 0.0068 (6) |
| C10 | 0.0443 (8) | 0.0596 (11) | 0.0674 (11) | 0.0127 (7) | 0.0233 (8) | 0.0043 (8) |
| C11 | 0.0517 (10) | 0.0963 (16) | 0.0527 (11) | −0.0182 (10) | 0.0053 (8) | −0.0141 (10) |
| C12 | 0.0449 (9) | 0.0990 (16) | 0.0484 (10) | 0.0056 (9) | 0.0017 (8) | 0.0119 (10) |
| C13 | 0.0529 (10) | 0.0562 (11) | 0.0935 (14) | −0.0131 (9) | 0.0175 (10) | −0.0120 (10) |
| C14 | 0.0375 (8) | 0.0825 (14) | 0.0785 (13) | −0.0044 (8) | 0.0194 (8) | −0.0032 (11) |
| C15 | 0.0540 (10) | 0.0724 (12) | 0.0452 (9) | 0.0086 (8) | 0.0183 (8) | 0.0043 (8) |
| C16 | 0.0905 (14) | 0.0552 (11) | 0.0627 (11) | 0.0198 (10) | 0.0256 (10) | 0.0137 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn—O1 | 2.0771 (12) | C6—H9 | 0.9800 |
| Zn—O2 | 2.0611 (11) | C6—H10 | 0.9800 |
| Zn—O3 | 2.0645 (11) | C6—C7 | 1.508 (2) |
| Zn—O4 | 2.0607 (10) | C7—C8 | 1.391 (3) |

| | | | |
|---|---|---|---|
| Zn—N1 | 2.2722 (13) | C8—H11 | 0.9500 |
| Zn—N2 | 2.2533 (13) | C8—C9 | 1.393 (2) |
| O1—C2 | 1.2509 (19) | C9—C10 | 1.507 (2) |
| O2—C4 | 1.2578 (19) | C10—H12 | 0.9800 |
| O3—C7 | 1.2619 (19) | C10—H13 | 0.9800 |
| O4—C9 | 1.2626 (17) | C10—H14 | 0.9800 |
| N1—C11 | 1.467 (2) | C11—H15 | 0.9900 |
| N1—C13 | 1.469 (2) | C11—H16 | 0.9900 |
| N1—C14 | 1.473 (2) | C11—C12 | 1.495 (3) |
| N2—C12 | 1.476 (2) | C12—H17 | 0.9900 |
| N2—C15 | 1.470 (2) | C12—H18 | 0.9900 |
| N2—C16 | 1.468 (2) | C13—H19 | 0.9800 |
| C1—H1 | 0.9800 | C13—H20 | 0.9800 |
| C1—H2 | 0.9800 | C13—H21 | 0.9800 |
| C1—H3 | 0.9800 | C14—H22 | 0.9800 |
| C1—C2 | 1.512 (2) | C14—H23 | 0.9800 |
| C2—C3 | 1.390 (2) | C14—H24 | 0.9800 |
| C3—H4 | 0.9500 | C15—H25 | 0.9800 |
| C3—C4 | 1.392 (2) | C15—H26 | 0.9800 |
| C4—C5 | 1.518 (2) | C15—H27 | 0.9800 |
| C5—H5 | 0.9800 | C16—H28 | 0.9800 |
| C5—H6 | 0.9800 | C16—H29 | 0.9800 |
| C5—H7 | 0.9800 | C16—H30 | 0.9800 |
| C6—H8 | 0.9800 | | |

| | | | |
|---|---|---|---|
| O1—Zn—O2 | 87.50 (4) | C7—C6—H8 | 109.5 |
| O1—Zn—O3 | 101.58 (5) | C7—C6—H9 | 109.5 |
| O1—Zn—O4 | 88.49 (4) | C7—C6—H10 | 109.5 |
| O1—Zn—N1 | 89.28 (5) | O3—C7—C6 | 115.59 (16) |
| O1—Zn—N2 | 168.94 (5) | O3—C7—C8 | 125.65 (15) |
| O2—Zn—O3 | 90.18 (5) | C8—C7—C6 | 118.76 (16) |
| O2—Zn—O4 | 175.16 (4) | C7—C8—H11 | 116.9 |
| O2—Zn—N1 | 93.76 (5) | C7—C8—C9 | 126.12 (15) |
| O2—Zn—N2 | 89.57 (5) | C9—C8—H11 | 116.9 |
| O3—Zn—O4 | 87.96 (4) | O4—C9—C8 | 125.48 (15) |
| O3—Zn—N1 | 168.61 (5) | O4—C9—C10 | 115.84 (15) |
| O3—Zn—N2 | 89.09 (5) | C8—C9—C10 | 118.67 (13) |
| O4—Zn—N1 | 88.92 (5) | C9—C10—H12 | 109.5 |
| O4—Zn—N2 | 94.86 (5) | C9—C10—H13 | 109.5 |
| N1—Zn—N2 | 80.27 (5) | C9—C10—H14 | 109.5 |
| C2—O1—Zn | 127.18 (11) | H12—C10—H13 | 109.5 |
| C4—O2—Zn | 126.86 (11) | H12—C10—H14 | 109.5 |
| C7—O3—Zn | 127.15 (11) | H13—C10—H14 | 109.5 |
| C9—O4—Zn | 127.15 (10) | N1—C11—H15 | 109.3 |
| C11—N1—Zn | 105.16 (10) | N1—C11—H16 | 109.3 |
| C11—N1—C13 | 110.51 (16) | N1—C11—C12 | 111.53 (16) |
| C11—N1—C14 | 110.95 (15) | H15—C11—H16 | 108.0 |
| C13—N1—Zn | 111.23 (10) | C12—C11—H15 | 109.3 |

| | | | |
|---|---|---|---|
| C13—N1—C14 | 107.86 (15) | C12—C11—H16 | 109.3 |
| C14—N1—Zn | 111.17 (11) | N2—C12—C11 | 111.49 (15) |
| C12—N2—Zn | 105.59 (11) | N2—C12—H17 | 109.3 |
| C15—N2—Zn | 111.69 (10) | N2—C12—H18 | 109.3 |
| C15—N2—C12 | 110.50 (15) | C11—C12—H17 | 109.3 |
| C16—N2—Zn | 111.08 (11) | C11—C12—H18 | 109.3 |
| C16—N2—C12 | 110.16 (14) | H17—C12—H18 | 108.0 |
| C16—N2—C15 | 107.84 (15) | N1—C13—H19 | 109.5 |
| H1—C1—H2 | 109.5 | N1—C13—H20 | 109.5 |
| H1—C1—H3 | 109.5 | N1—C13—H21 | 109.5 |
| H2—C1—H3 | 109.5 | H19—C13—H20 | 109.5 |
| C2—C1—H1 | 109.5 | H19—C13—H21 | 109.5 |
| C2—C1—H2 | 109.5 | H20—C13—H21 | 109.5 |
| C2—C1—H3 | 109.5 | N1—C14—H22 | 109.5 |
| O1—C2—C1 | 116.12 (15) | N1—C14—H23 | 109.5 |
| O1—C2—C3 | 126.06 (16) | N1—C14—H24 | 109.5 |
| C3—C2—C1 | 117.82 (15) | H22—C14—H23 | 109.5 |
| C2—C3—H4 | 117.4 | H22—C14—H24 | 109.5 |
| C2—C3—C4 | 125.30 (15) | H23—C14—H24 | 109.5 |
| C4—C3—H4 | 117.4 | N2—C15—H25 | 109.5 |
| O2—C4—C3 | 126.43 (15) | N2—C15—H26 | 109.5 |
| O2—C4—C5 | 115.53 (15) | N2—C15—H27 | 109.5 |
| C3—C4—C5 | 118.02 (15) | H25—C15—H26 | 109.5 |
| C4—C5—H5 | 109.5 | H25—C15—H27 | 109.5 |
| C4—C5—H6 | 109.5 | H26—C15—H27 | 109.5 |
| C4—C5—H7 | 109.5 | N2—C16—H28 | 109.5 |
| H5—C5—H6 | 109.5 | N2—C16—H29 | 109.5 |
| H5—C5—H7 | 109.5 | N2—C16—H30 | 109.5 |
| H6—C5—H7 | 109.5 | H28—C16—H29 | 109.5 |
| H8—C6—H9 | 109.5 | H28—C16—H30 | 109.5 |
| H8—C6—H10 | 109.5 | H29—C16—H30 | 109.5 |
| H9—C6—H10 | 109.5 | | |