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# Synthesis of thiolate and phosphido bridged iron–manganese complexes; molecular structure of *cis*-[FeMn(μ-CO)(μ-SEt)(CO)$_2$(Cp)(C$_5$H$_4$Me)][☆]

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## Abstract

The reaction of [Fe(CO)$_2$(SR)(Cp)] (R = Et, Ph; Cp = η-C$_5$H$_5$) with [Mn(CO)$_2$(thf)(C$_5$H$_4$Me)] (thf = tetrahydrofuran), under photolytic conditions, leads to the formation of the novel heterodinuclear bridged thiolate complexes [FeMn(μ-CO)(μ-SR)(CO)$_2$(Cp)(C$_5$H$_4$Me)] in low yields. [FeMn(μ-CO)(μ-SEt)(CO)$_2$(Cp)(C$_5$H$_4$Me)] consists of a mixture of *cis* and *trans* isomers which have been separated and characterized by IR and NMR spectroscopy. The μ-phosphido complex [FeMn(μ-CO)(μ-PPh$_2$)(CO)$_2$(Cp)(C$_5$H$_4$Me)] has been prepared analogously from [Fe(CO)$_2$(PPh$_2$)(Cp)] and [Mn(CO)$_2$(thf)(C$_5$H$_4$Me)]. Variable temperature NMR spectra of the latter heterodinuclear complex, in CDCl$_3$, show the presence of an equilibrium mixture of the two interconverting *cis* and -*trans* isomers. The X-ray molecular structure of *cis*-[FeMn(μ-CO)(μ-SEt)(CO)$_2$(Cp)(C$_5$H$_4$Me)] shows a bonded Fe–Mn interaction [2.617(2) Å] reinforced by a μ-CO and a μ-SEt ligands. The molecule contains chiral centers at the iron, manganese and sulfur atoms and the diastereoisomer under study exhibits optimized non bonded contacts between the alkyl groups.

*Keywords:* Dinuclear; Iron–manganese; Carbonyl complexes; μ-Thiolate; μ-Phosphido; Crystal structure

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## 1. Introduction

Heterodinuclear organometallic compounds are an area of active interest [1] because bonded M–M′ units can cooperate in producing new and distinct reactivity patterns [2]. Bridging ligands are introduced frequently in order to prevent breaking of the metal–metal bond, although growing interest is placed in heterobimetallic unbridged compounds [3]. Our work in the area has led to the synthesis and structural characterization of the thiocarbonyl compound [FeMn(μ-CO)(μ-CS)(CO)$_5$(Cp)] [4] and the dinuclear W–M (M = Cu, Ag, Au) complexes, in which the metal–metal bond is bridged by aminocarbyne ligands [5]. Since only few other examples of Fe–Mn complexes containing bridging ligands are known [6], including bridging phosphido species [7], we have extended our work with the aim of obtaining new Fe–Mn complexes containing bridging thiolato and phosphido ligands.

Herein we report on the synthesis, spectroscopic characterization and stereochemistry of novel iron–manganese complexes [FeMn(μ-CO)(μ-X)(CO)$_2$(Cp)-(C$_5$H$_4$Me)] (X = SEt, SPh and PPh$_2$). The X ray molecular structure of the –SEt derivative is described.

## 2. Results and discussion

Addition of [Fe(CO)$_2$(SEt)(Cp)] [8] to a thf solution of [Mn(CO)$_2$(thf)(C$_5$H$_4$Me)] (thf = tetrahydrofuran) re-

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[☆] The authors wish to dedicate the publication to Professor Alberto Ceccon on the occasion of his 65th birthday.

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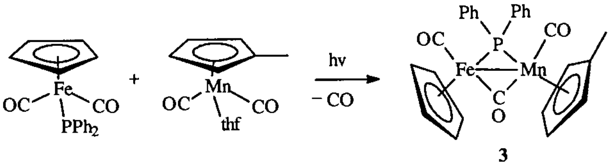
reach the eighteen electrons configuration. The crystal structure analysis indicates that the doubly bridged Fe–Mn bond [2.617(2) Å] (Table 1) is slightly longer than the Fe–Fe interaction in the analogous homonuclear complex [$Fe_2$(μ-CO)(μ-SEt)$(CO)_2(Cp)_2$][$BPh_4$] [2.580(2) Å] [14] but shorter than the Mn–Mn distances in the singly bridged *trans*-[$Mn_2$(μ-CO)(μ-SEt)$(CO)_2$-$(C_5H_4Me)]^+$ [2.930(1) Å] [13a] and [(Cp)Mn(CO)(μ-CO)(μ-S–$tC_4H_9$)Mn$(CO)_4$] [2.782(2) Å] [15]. The Fe–S–Mn–C(1) diamond is close to planarity [dihedral angle between the Fe–Mn–S and Fe–Mn–C(1) planes 13.5(3)°]. Of the two bridging ligands the ethylthiolate is almost symmetric [Fe–S, 2.194; Mn–S, 2.210(2) Å], whereas the bridging carbonyl shows some asymmetry [Mn–C(1), 1.909; Fe–C(1) 2.017(5) Å]. In view of the fact that the σ good donor thiolate ligand establishes substantially symmetric interactions with the two metal atoms, one could speculate that the asymmetry exhibited by the bridging carbonyl ligand is a π bonding effect; i.e. the π Mn–CO interaction is stronger than the corresponding Fe–CO back-donation, in accord with the attribution of a lower oxidation state to the manganese.

The reaction of [Mn$(CO)_2$(thf)$(C_5H_4Me)$] with [Fe$(CO)_2$(SPh)(Cp)], freshly generated from [(Cp)Fe-$(CO)_2$(thf)]$SO_3CF_3$ and NaSPh, occurs as previously described for the synthesis of **1**, affording [FeMn(μ-CO)(μ-SPh)$(CO)_2$(Cp)$(C_5H_4Me)$] **2** in about 13% yield. Unlike compound **1**, which was obtained in both *cis* and *trans* isomeric forms, the μ-phenyl thiolate complex **2** has been isolated, from column chromatography, only as *cis*-isomer. Its characterization was straightforward since its spectroscopic properties closely resemble those of *cis*-**1** (see experimental part).

The synthetic procedure described by Scheme 1 can be placed in the category of the 'bridge-assisted' reactions in which the thiolate ligand serves to bring the metals together [1a]. In the same way, terminal phosphido metal complexes have been shown to be good precursors for the preparation of hetero-bimetallic compounds [16], including Fe–Mn complexes [7b]. As a matter of fact the reaction of [Fe$(CO)_2$($PPh_2$)(Cp)] [17] with [Mn$(CO)_2$(thf)$(C_5H_4Me)$], under photholitic conditions, affords [FeMn(μ-CO)(μ-$PPh_2$)$(CO)_2$(Cp)$(C_5H_4$-Me)] **3** in about 23% yield (Scheme 2), together with minor amounts of [$Fe_2(CO)_4(Cp)_2$] and [Mn$(CO)_3$-$(C_5H_4Me)$].

Table 1
Selected bond lengths (Å) and angles (°) for [FeMn(μ-CO)(μ-SEt)$(CO)_2$(Cp)$(C_5H_4Me)$]

| | | | |
|---|---|---|---|
| Fe–Mn | 2.617(2) | Fe–C(2) | 1.743(5) |
| Fe–S | 2.194(2) | C(2)–O(2) | 1.149(6) |
| Mn–S | 2.210(2) | Mn–C(3) | 1.761(5) |
| S–C(4) | 1.821(5) | C(3)–O(3) | 1.136(6) |
| Mn–C(1) | 1.909(5) | C(4)–C(5) | 1.509(8) |
| Fe–C(1) | 2.017(5) | Fe–C($C_5H_5$) | 2.116 |
| C(1)–O(1) | 1.165(6) | Mn–C($C_5H_4$Me) | 2.133 |
| Fe–S–Mn | 72.92(6) | C(4)–S–Mn | 114.8(2) |
| C(4)–S–Fe | 113.2(2) | | |



Scheme 2.

Compound **3** has been separated by column chromatography and purified by crystallization. Variable-temperature NMR spectra of **3** suggest that this compound exists in solution as interconverting *cis-trans* isomers. Low temperature (233 K) $^1$H-NMR spectra in $CDCl_3$ exhibits distinct patterns for the *cis* and *trans* isomers, which are present in about the same ratio. Two resonances at 4.67 and 4.51 ppm are observed for the Cp ligand, and two $C_5H_4Me$ methyl peaks occur at 2.16 and 2.14 ppm. The $C_5H_4Me$ ring hydrogens originate eight distinct signals in the 4.88–3.62 ppm range due to the non coincidence of the *cis-trans* isomers and to the fact that they are diastereotopic. Rising the temperature results in broadening and coalescence (at about 280 K) of all the signals. Heating the sample to 313 K results in the observation of a single sharp resonance for the Cp (at 4.55 ppm) and for the $C_5H_4Me$ methyl signal (at 2.10 ppm). At that temperature the resonances due to the $C_5H_4Me$ ring protons remain broad, except for some sharpening of a signal at about 4.02 ppm. Return to low temperature gives the same ratio of isomers as at the start. However the ratio becomes about 1: 0.6 (measured for the Cp resonances at 4.99 and 4.98 ppm) in deuterated acetone solution, (at 233 K) where the more polar *cis*-isomer is presumably favoured. The observed temperature dependent behaviour is consistent with *cis-trans* isomerization, as seen for the analogous Fe–Mn complex [FeMn(μ-CO)(μ-COR)$(CO)_2$(Cp)$(C_5H_4Me)$] (R = Me, Et) [12]. In the latter case interconversion of the isomers was suggested to occur *via* ring-opening, rotation around the metal-metal bond and closure of the bridging ligand. Isomerization of *cis-trans* **3** could be analogous although we can not exclude alternative mechanisms in which the phosphido bridge remains intact and openings involve μ-CO and the metal–metal bond [18]. The presence of two isomeric forms is also evidenced in the low temperature $^{13}$C-NMR spectrum of **3**, by the appearance of two sets of peaks of about the same intensity for each resonance (e.g. for the Cp carbons at 87.8 and 85.5 ppm, the $C_5H_4Me$ methyl carbons at 14.4 and 13.7 ppm, the FeCO at 213.9 and 212.8 ppm, the MnCO at 230.1 and 228.8 ppm).

The IR spectrum of **3** shows, in the CO region, bands due to terminally bonded CO (1957s, 1937sh, 1894s, $cm^{-1}$) and one bridging $\nu$-CO (1762m $cm^{-1}$). The relative intensities of the absorptions changes in less polar solvents (e.g. hexane: 1974w, 1941m 1903s and 1787m $cm^{-1}$) that is consistent with the presence of an equilibrium mixture of the two interconverting *cis* and *trans* isomers, the first being favoured in more polar solvents.

Finally, it should be mentioned that the reactions of **3** with $HSO_3CF_3$ and $MeSO_3CF_3$ have been investigated. Both protonation and methylation occur at the P atom promoting bridge opening and Fe–Mn fragmentation, suggesting that the phosphido bridge largely contributes to the stability of **3**. The compounds $[Fp(PHPh_2)]SO_3CF_3$ ($Fp = Fe(CO)_2(Cp)$) [19] and $[Fp(PMePh_2)]SO_3CF_3$ [20] have been identified among the products of the reaction of **3** with $HSO_3CF_3$ and $MeSO_3CF_3$, respectively, whereas it is still unknown the fate of the Mn fragment.

## 3. Experimental

### 3.1. General

All reactions were carried out routinely under argon using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin–Elmer 983-G spectrophotometer, $^1$H- and $^{13}$C-NMR spectra on a Varian Gemini 300. The shiftless relaxation reagent $[Cr(acac)_3]$ (acac = acetylacetonate) was added to solution studied by $^{13}$C-NMR spectroscopy. All reagents were commercial products (Aldrich) of the highest purity available and used as received. Compound $[Mn(CO)_2(thf)(C_5H_4Me)]$ was prepared in situ by irradiating a thf solution of $[Mn(CO)_3(C_5H_4Me)]$ under a stream of Ar. Compounds $[Fe(CO)_2(SR)(Cp)]$ (R = Et, Ph) were obtained with a slight modification of the procedure described in the literature [8].

### 3.2. Synthesis of $[FeMn(\mu\text{-}CO)(\mu\text{-}SEt)(CO)_2(Cp)(C_5H_4Me)]$ 1

A thf (20 ml) solution of $[Fe(CO)_2(SEt)(Cp)]$ (3.55 mmol), freshly prepared from $[Fe(CO)_2(thf)(Cp)]SO_3CF_3$ and NaSEt, was transferred, by cannula, into a UV immersion lamp reactor containing $[Mn(CO)_2(thf)(C_5H_4Me)]$ which has been obtained by irradiating $[Mn(CO)_3(C_5H_4Me)]$ (1.13 g, 5.18 mmol) in thf (200 ml). The mixture was stirred for 1 h and the resulting dark-brown solution was photolyzed for 30 min under a stream of Argon. Further stirring for 1 h and filtration on an allumina pad gave a brown solution which was evaporated to dryness under vacuum. The residue was chromatographed on an alumina column (5 × 30 cm) with $Et_2O$:Petroleum ether (b.p. 40–70°C) 1:3 (v/v) as eluent. A first fraction, containing some unreacted $[Mn(CO)_3(C_5H_4Me)]$ was discharged. A second yellow–brown fraction was collected, evaporated to dryness and crystallized from $CH_2Cl_2$ layered with n-pentane at −20°C affording $[Fe(CO)(SEt)(Cp)]_2$ (66 mg, 9% yield) which was identified by comparison with the spectroscopic properties reported in the literature [8,9]. Further elution gave a red fraction that was collected and evaporated to dryness affording *trans*-**1**. Yield (148 mg, 10%). Analysis. Found: C, 48.02; H, 4.24%. $C_{16}H_{17}FeMnO_3S$ requires: 48.03; H, 4.28%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1952m, 1899s and 1776m (CO). NMR: $\delta_H$ ($CDCl_3$): 4.78 (5 H, s, CpFe), 4.53, 4.45, 4.39, 4.32 (4 H, s, $MeC_5H_4Mn$), 3.16 (1 H, m, $SCH_2CH_3$), 2.09 (1 H, m, $SCH_2CH_3$), 1.92 (3 H, s, $MeC_5H_4Mn$) and 1.54 (3 H, t, $SCH_2CH_3$) ppm. $\delta_C$ ($CDCl_3$): 268.7 (μ-CO), 230.0 (Mn–CO), 212.7 (Fe–CO), 105.6, 89.2, 88.5, 87.6, 84.5 ($MeC_5H_4Mn$), 86.6 (CpFe), 39.2 ($SCH_2CH_3$), 19.0 ($SCH_2CH_3$) and 13.6 ($MeC_5H_4Mn$) ppm.

Finally, a green-brown fraction was collected, evaporated to dryness and crystallized from $Et_2O$ layered with n-pentane at −20°C yielding *cis*-**1** (0.45 g, 32%). Analysis. Found: C, 48.10; H, 4.22%. $C_{16}H_{17}FeMnO_3S$ requires: C, 48.03; H, 4.28%. IR ($CH_2Cl_2$) $\nu_{max}$($cm^{-1}$) 1958s, 1897m and 1774m (CO). NMR: $\delta_H$ ($CDCl_3$): 4.70 (5 H, s, CpFe), 4.39, 4.31, 4.10 (4 H, s, $MeC_5H_4Mn$), 2.35 (2 H, m, $SCH_2CH_3$), 2.10 (3 H, s, $MeC_5H_4Mn$) and 1.45 (3 H, t, $SCH_2CH_3$) ppm. $\delta_C$ ($CDCl_3$): 269.0 (μ-CO), 229.7 br (Mn–CO), 213.4 (Fe–CO), 103.7, 87.2, 87.1, 85.9, 85.6 ($MeC_5H_4Mn$), 84.4 (CpFe), 38.6 ($SCH_2CH_3$), 19.3 ($SCH_2CH_3$) and 13.9 ($MeC_5H_4Mn$) ppm.

### 3.3. Synthesis of $[FeMn(\mu\text{-}CO)(\mu\text{-}SPh)(CO)_2(Cp)(C_5H_4Me)]$ 2

Complex **2** was obtained following the same procedure described for the preparation of **1** starting from $[Fe(CO)_2(SPh)(Cp)]$ (2.4 mmol), prepared from $[Fe(CO)_2(Cp)(thf)]$ and NaSPh, and a slight excess of $[Mn(CO)_2(thf)(C_5H_4Me)]$ (3.0 mmol). Yield (145 mg, 13%). Analysis. Found: C, 53.46; H, 3.90%. $C_{20}H_{17}FeMnO_3S$ requires: C, 53.60; H, 3.82%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1968s, 1905m and 1774m (CO). NMR: $\delta_H$ ($CD_2Cl_2$): 7.65–7.00 (5 H, m, SPh), 4.83 (5 H, s, Cp), 4.77–4.40 (4 H, m, $MeC_5H_4Mn$) and 2.16 (3

H, s, $MeC_5H_4Mn$) ppm. $\delta_C$ ($CD_2Cl_2$): 267.1 ($\mu$-CO), 229.2 (Mn–CO), 212.9 (Fe–CO), 146.8, 133.0, 128.1, 127.1 (Ph), 104.5, 88.1, 87.8, 86.7, 86.2 ($Me\mathit{C}_5H_4Mn$), 84.9 (CpFe) and 14.4 ($\mathit{Me}C_5H_4Mn$) ppm.

### 3.4. Synthesis of [FeMn ($\mu$-CO)($\mu$-$PPh_2$)$(CO)_2$(Cp)-($C_5H_4Me$)] **3**

Complex **3** was obtained following the same procedure described for the preparation of **1** using [$Fe(CO)_2(PPh_2)(Cp)$] (2.8 mmol), prepared from [$Fe(CO)_2$(thf)(Cp)] and $LiPPh_2$, in place of [$Fe(CO)_2$(SEt)(Cp)] and a slight excess of [$Mn(CO)_2$(thf)($C_5H_4Me$)] obtained by photolysis of [$Mn(CO)_3(C_5H_4Me)$] (0.70 g, 3.2 mmol). Chromatography of the reaction products on alumina column, with $CH_2Cl_2$-hexane as eluent (1:3, v/v) gave a first yellow fraction of [$Mn(CO)_3(C_5H_4Me)$] (0.18 g) was followed by some [$Fe_2(CO)_4(Cp)_2$]. Further elution with thf gave third reddish-brown fraction of **3** which was collected and crystallized at −20°C from $CH_2Cl_2$ layered with n-pentane. (Yield 0.34 g, 23%). Analysis. Found: C, 59.67; H, 4.31%. $C_{26}H_{22}FeMnO_3S$ requires: C, 59.57; H, 4.23%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1957s, 1937sh, 1894s and 1762s (CO). NMR: $\delta_H$ ($CDCl_3$, 233 K): 7.71–6.98 (10 H, m, Ph), 4.67, 4.51 (5 H, s, CpFe), 4.88, 4.77, 4.75, 4.30, 4.14, 3.94, 3.88, 3.62 (3 H, s, $MeC_5\mathit{H}_4Mn$), 2.16 and 2.06 (3 H, s, $\mathit{Me}C_5H_4Mn$) ppm; *cis*-*trans* isomers in about 1:1 ratio; ($CDCl_3$, 295 K): 7.70–7.32 (10 H, m, Ph), 4.55 ( ~ 5 H, s br, CpFe), 4.75, 3.95, 3.70 (s, br $MeC_5\mathit{H}_4Mn$) 4.02 ( ~ 1 H, s, br $MeC_5\mathit{H}_4Mn$) and 2.10 ( ~ 3 H, s, br, $\mathit{Me}C_5H_4Mn$). $\delta_H$ ($CDCl_3$, 313 K): 7.70–7.31 (10 H, m, Ph), 4.55 ( ~ 5 H, s, *Cp*Fe), 4.01 ( ~ 1 H, s, br $MeC_5\mathit{H}_4Mn$), (3 H, m, $Me\mathit{C_5H_4}Mn$), and 2.10 (3 H, s, $\mathit{Me}C_5H_4Mn$) ppm. $\delta_C$ ($CDCl_3$, 253 K) *cis* and *trans* isomers: 275.6, 274.4 (μ-CO), 230.1 (d, $J_{CP}=19.4$ Hz), 228.8 (d, $J_{CP}=19.4$ Hz) (Mn–CO), 213.9 (d, $J_{CP}=15.0$ Hz), 212.8 (d, $J_{CP}=16.3$ Hz) (Fe–CO), 137.0–128.3 (m, Ph), 103.3, 101.1, 89.7, 89.2, 88.2, 86.4, 85.9, 85.6, 84.6 ($Me\mathit{C}_5H_4Mn$), 87.8, 85.5 (*Cp*Fe), 14.4, and 13.7 ($\mathit{Me}C_5H_4Mn$) ppm. $\delta_P$ ($CDCl_3$, 295 K) *cis* and *trans* isomers: ($CDCl_3$) 300 Mhz: 219.6, and 209.7 ppm. MS m/e: 524 ($M^+$), 496 (–CO), 468 (–2CO), 448 (–3CO, base peak).

### 3.5. X-ray structure determination of [FeMn($\mu$-CO)($\mu$-SEt)$(CO)_2$(Cp)($C_5H_4Me$)] **1**

Crystal data and details of the data collection for [FeMn(μ-CO)(μ-SEt)$(CO)_2$(Cp)($C_5H_4Me$)] are given in Table 2. The diffraction experiments were carried out at 200 K on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo–$K_\alpha$ radiation. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. No decay correction was necessary. An empirical absorption correction was applied by using the azimuthal scan method [21]. The positions of the metal atoms were found by direct methods using the SHELXS 86 program [22] and all the non-hydrogen atoms located in Fourier syntheses. The hydrogen atoms were located in successive Fourier-difference maps but added in calculated positions and allowed to ride the pertinent carbon atoms during the refinement. Although manganese and iron atoms were recognized unambigously by the non equivalence of their chemical environments a refinement was made with inverted assignement of the metal atoms. Interestingly, this calculation gave an $R$ factor of 0.0504 against 0.0474 of the correct structure. Our data were therefore able to discriminate contiguous metal atoms in the periodic table. The final refinement on $F^2$ proceeded by full-matrix least-squares calculations (SHELXL 93) [23] using anisotropic thermal parameters for all the non-hydrogen atoms. The methyl and methylene H atoms were assigned an isotropic thermal parameter 1.3 times $U_{eq}$ of the carbon atoms to which they were attached. In the final difference Fourier synthesis the electron density was found in the range −0.66 to 0.92 e Å$^{-3}$. A

Table 2
Crystal data and experimental details for [FeMn(μ-CO)(μ-SEt)$(CO)_2$(Cp)($C_5H_4Me$)]

| | |
|---|---|
| Formula | $C_{16}H_{17}FeMnNO_3S$ |
| Formula weight | 400.15 |
| Temperature (K) | 200(2) |
| Wavelength (Å) | 0.71069 |
| Crystal symmetry | Triclinic |
| Space group | $P\bar{1}$ (No. 2) |
| *Unit cell dimensions* | |
| $a$ (Å) | 6.732(6) |
| $b$ (Å) | 9.303(8) |
| $c$ (Å) | 13.261(6) |
| $\alpha$ (°) | 80.35(2) |
| $\beta$ (°) | 83.33(3) |
| $\gamma$ (°) | 82.98(2) |
| Cell volume (Å$^3$) | 809(1) |
| $Z$ | 2 |
| $D_c$ (Mg m$^{-3}$) | 1.643 |
| μ(Mo–$K_\alpha$) (mm$^{-1}$) | 1.814 |
| $F$(000) | 408 |
| Crystal size (mm) | 0.20 × 0.25 × 0.30 |
| $\theta$ limits (°) | 2–27 |
| Scan mode | ω |
| Reflections collected | 3506 ($\pm h$, $\pm k$, $+l$) |
| Unique observed reflections [$F_o > 4\sigma(F_o)$] | 2489 |
| Goodness of fit on $F^2$ | 1.050 |
| $R_1$ ($F$) [a], $wR_2$ ($F^2$) [b] | 0.0474, 0.1269 |
| Weighting scheme | $a=0.0728$,<br>$b=1.2486$ [b] |
| Largest difference peak and hole, (e Å$^{-3}$) | 0.916 and −0.656 |

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$.

complete list of bond lengths and angles and a table of anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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