X-ray-determined structure of the technetium complex [Tc$_2$(μ-CO)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] revisited: [Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] as the correct formulation

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X-ray-determined structure of the technetium complex [Tc$_2$(μ-CO)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] revisited: [Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] as the correct formulation

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Some of us reported previously the structure of di-μ-carbonyl-bis[tricarbonyl(pyridine)technetium], [Tc$_2$(μ-CO)$_2$(C$_5$H$_5$N)$_2$(CO)$_6$], as the main product of the reaction of [Tc$_2$(CO)$_{10}$] with pyridine at room temperature, using the reagent itself as solvent [Zuhayra *et al.* (2008). *Inorg. Chem.* **47**, 10177–10182]. On the basis of an X-ray analysis of the product, a molecular structure was proposed with two bridging carbonyls displaying very unusual geometrical features, not explained at the time. Subsequent chemical considerations, coupled with density functional theory (DFT) calculations, prompted us to revise the original structure determination. Using the original raw diffraction data, we have now performed new refinements to show that the previously proposed 'bridging carbonyls' actually correspond to bridging methoxide groups, and that the crystals analyzed at the time therefore would correspond to the complex di-μ-methoxido-bis[tricarbonyl(pyridine)technetium], *syn*-[Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$]. This methoxide-bridged complex likely was a minor side product formed along with the main product in the above reaction, perhaps due to the presence of trace amounts of methanol and air in the reaction mixture.

1. Introduction

Some of us reported previously that the room-temperature reaction of [Tc$_2$(CO)$_{10}$] with pyridine, using the reagent itself as solvent, yields the octacarbonyl complex [Tc$_2$(NC$_5$H$_5$)$_2$(CO)$_8$] (**1**) as the unique product, which upon heating undergoes an interesting C—H bond cleavage of a pyridine molecule (Zuhayra *et al.*, 2008). On the basis of an X-ray analysis of the above product, a molecular structure was proposed for isomer *syn*-**1** with two bridging carbonyls displaying several unusual geometrical features not explained at the time (Fig. 1): (i) a strong pyramidalization of the bridgehead C atoms, with unusually small displacement parameters and very large C—O separations of *ca* 1.45 Å, actually close to the reference value of 1.42 Å for a C(sp^3)—O single bond (Cordero *et al.*, 2008), and far larger than the reference value of 1.21 Å for a double bond between these atoms (Pyykkö & Atsumi, 2009); and (ii) a large intermetallic separation of *ca* 3.37 Å, far above that of the parent complex [Tc$_2$(CO)$_{10}$] (*ca* 3.03 Å; Bailey & Dahl, 1965; Sidorenko *et al.*, 2011), and inconsistent with the formulation of a single Tc—Tc bond, as required by application of the 18-electron rule to complex *syn*-**1**. Recently, we used density functional theory (DFT) calculations to find that the most likely structure of **1** would display only terminal carbonyls and a staggered conformation,
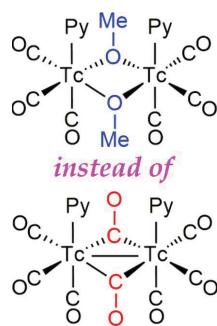
Table 1
Experimental details for structural determinations of complexes *syn*-**1** to *syn*-**3**.

	syn-**1**[a]	*syn*-**2**	*syn*-**3**
Crystal data			
Chemical formula	$C_{18}H_{10}N_2O_8Tc_2$	$C_{16}H_{12}N_2O_{10}Tc_2$	$C_{18}H_{16}N_2O_8Tc_2$
M_r	578.28	588.28	584.33
Crystal system, space group	Orthorhombic, $Pna2_1$	Orthorhombic, $Pna2_1$	Orthorhombic, $Pna2_1$
Temperature (K)	200	200	200
a, b, c (Å)	18.116 (16), 10.359 (8), 12.148 (10)	18.116 (16), 10.359 (8), 12.148 (10)	18.116 (16), 10.359 (8), 12.148 (10)
V (Å^3)	2280 (3)	2280 (3)	2280 (3)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.25	1.26	1.26
Crystal size (mm)	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.2$
Data collection			
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2614, 2614, 2265	2614, 2614, 2265	2614, 2614, 2265
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.639	0.639	0.639
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.146, 1.10	0.046, 0.122, 1.05	0.042, 0.113, 1.05
No. of reflections	2614	2614	2614
No. of parameters	273	281	274
No. of restraints	1	4	1
H-atom treatment	Only H-atom displacement parameters refined	Only H-atom displacement parameters refined	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.16, −1.14	1.12, −0.97	1.13, −1.03
Flack parameter	0.07 (10)	0.04 (9)	0.02 (8)

Note: (*a*) data taken from Zuhayra *et al.* (2008). Computer programs: *SHELXL2017* (Sheldrick, 2015*b*) in *WinGX* (Farrugia, 2012), *SHELXT2014* (Sheldrick, 2015*a*) and *OLEX2* (Dolomanov *et al.*, 2009).

as observed in the parent precursor, and that the crystals analysed by X-ray diffraction in 2008 would most likely correspond to either the hydroperoxide-bridged ditechnetium(I) complex *syn*-[Tc$_2$(μ-OOH)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] (*syn*-**2**) or its methoxide-bridged analogue *syn*-[Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] (*syn*-**3**) (García-Vivó & Ruiz, 2020). This prompted us to revise the structure determination of compound *syn*-**1** by performing new refinements using the original raw diffraction data, which is the purpose of the present article. As will be shown below, the new refinements indicate beyond doubt that the crystal actually analyzed at the time was not that of compound *syn*-**1** but that of the methoxide-bridged complex *syn*-[Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] (*syn*-**3**), whereby the 'anomalous' geometrical parameters mentioned above now become 'as expected'.

2. Experimental

Diffraction data were collected on a Siemens Nicolet Syntex R3m/V diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Intensities were measured by fine-slicing φ-scans and corrected for background, polarization and Lorentz effects. The original structure of *syn*-**1** was solved by direct methods and refined with the programs *SHELXS86* and *SHELXL93* (Sheldrick, 2008) by a full-matrix least-squares method based on F^2 (Zuhayra *et al.*, 2008).

Taking the same diffraction data, the structures of *syn*-**2** and *syn*-**3** were now solved by a dual-space algorithm using *SHELXT2014* (Sheldrick, 2015*a*) and refined by full-matrix

least-squares on F^2 using *SHELXL2017* (Sheldrick, 2015*b*) within *OLEX2* (Dolomanov *et al.*, 2009) and *WinGX* (Farrugia, 2012) environments.

2.1. Refinement

Crystal data, data collection and structure refinement details for *syn*-**1**, *syn*-**2** and *syn*-**3** are summarized in Table 1. All carbon-bound H atoms were calculated at their optimal positions and treated as riding on their parent atoms using isotropic displacement parameters 1.2 (or 1.5 in the case of methyl groups) times larger than the U_{eq} values of the respective parent atoms. The methyl groups in *syn*-**3** were calculated as idealized rotating groups. We could not recover

Table 2
Selected parameters (Å, Å^2) for structural determinations following formulations as *syn*-**1** to *syn*-**3**.

Parameter	*syn*-**1**[a] (XY = CO)	*syn*-**2** (XY = OO)	*syn*-**3** (XY = OC)
Tc···Tc	3.370 (3)	3.369 (3)	3.368 (3)
Average Tc—(μ-X)	2.163	2.162	2.163
$X4$—$Y4$	1.451 (14)	1.441 (12)	1.424 (11)
$X5$—$Y5$	1.470 (14)	1.433 (14)	1.415 (11)
$U_{eq}(X4)$	0.018 (2)	0.034 (2)	0.035 (2)
$U_{eq}(X5)$	0.019 (1)	0.037 (2)	0.038 (1)
$U_{eq}(Y4)$	0.083 (3)	0.082 (3)	0.044 (2)
$U_{eq}(Y5)$	0.112 (5)	0.116 (5)	0.061 (3)
ΔMSDA($X4$—$Y4$)	0.052 (8)	0.036 (8)	0.010 (6)
ΔMSDA($X5$—$Y5$)	0.040 (11)	0.041 (11)	0.008 (7)

Note: (*a*) data taken from Zuhayra *et al.* (2008).

from the stored old data (recorded some 20 years ago) all the information currently required for standard CIF files, and this caused the appearance of some A-level alerts in the corresponding *checkCIF* reports for **syn-2** and **syn-3**.

3. Results and discussion

The small size of the displacement ellipsoids of the bridgehead 'carbon' atoms (C4 and C5) in the original structure determination of **syn-1**, compared to those of the corresponding O atoms (O4 and O5; Fig. 1 and Table 2), suggested that positions C4 and C5 might actually correspond to atoms having a higher number of electrons (Stout & Jensen, 1989). Moreover, the theoretical calculations mentioned above indicated that replacing the bridging carbonyl ligands in **syn-1** with either


(a)

(b)
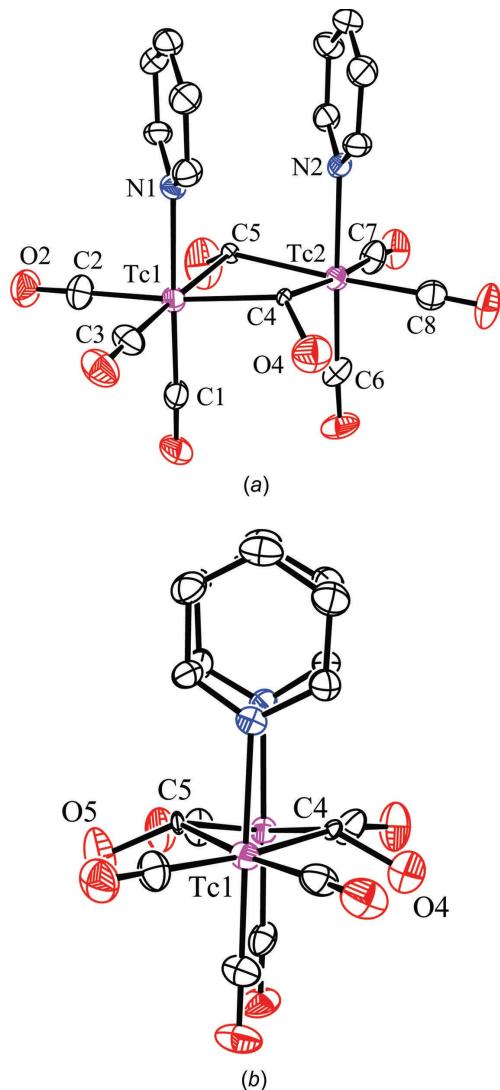
Figure 1
(a) The molecular structure (30% probability displacement ellipsoids) of the presumed compound **syn-1**, with H atoms omitted for clarity. (b) A view of the molecule along an axis close to the intermetallic line (García-Vivó & Ruiz, 2020). Both images were generated from the original CIF file (Zuhayra *et al.*, 2008). Selected bond lengths (Å): Tc1···Tc2 = 3.370 (3), C1—O1 = 1.148 (13), C2—O2 = 1.14 (2), C3—O3 = 1.149 (15), C4—O4 = 1.451 (14) and C5—O5 = 1.470 (14).

(a)

(b)
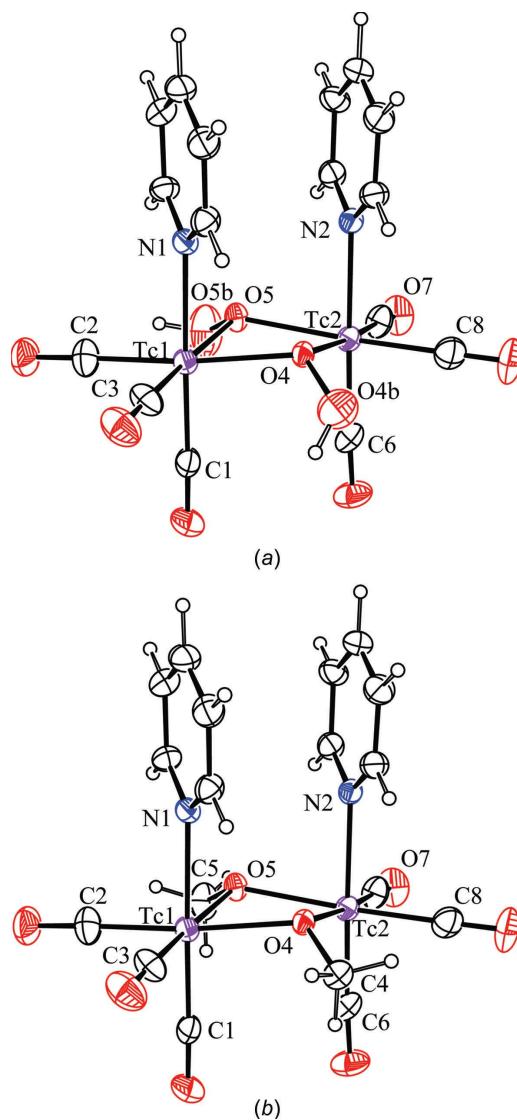
Figure 2
The molecular structure (30% probability displacement ellipsoids) following formulations as (a) **syn-2** and (b) **syn-3**.

OOH (peroxide) or OMe (methoxide) groups would yield complexes with geometries matching the anomalous features of the original structural determination (García-Vivó & Ruiz, 2020). We then proceeded to make new refinements with the original raw diffraction data under both hypotheses (**syn-2** and **syn-3**, respectively). Both refinements converged satisfactorily to give improved fitting parameters, compared to the original refinement based on the formulation syn-[Tc$_2$(μ-CO)$_2$(N-C$_5$H$_5$)$_2$(CO)$_6$] (Fig. 2, and Tables 1 and 2), but there were some significant differences between them: (i) the R_1, wR_2 and goodness-of-fit (GOF) values were better for **syn-3**. (ii) the U_{eq} values for the heavy atoms at the bridging positions (OO or OC) were more similar to each other in the case of **syn-3**; in contrast, the U_{eq} values for the O(H) atoms in **syn-2** were almost three times the value of the corresponding bridgehead O atom. This is clearly reflected in the significantly smaller values of *ca* 0.01 Å^2 in the difference between the mean-square displacement amplitudes (ΔMSDA) for the C4/O4 or

C5/O5 pairs in **syn-3**, as expected for mutually bonded atoms (Hirshfeld, 1976), which can be compared with values of *ca* 0.04 Å^2 for the corresponding pairs in either **syn-2** or **syn-1** (Table 2). Moreover, we note that the average C—O bond length for the bridging methoxide groups in **syn-3** (*ca* 1.42 Å) exactly matches the reference value for a $C(sp^3)$—O single bond. In contrast, the average O—O bond length of 1.43 Å in the formulation as **syn-2** falls below the values of 1.45–1.50 Å typically determined for OO*R*-bridged complexes (García-Vivó & Ruiz, 2020). All of this provides conclusive evidence for the presence of methoxide groups bridging the Tc atoms in the complex under discussion. It is thus concluded that the crystal analyzed at the time actually was not one of compound **syn-1** but one of the methoxide-bridged complex syn-[Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] (**syn-3**). We finally note that the geometrical parameters obtained for this complex are similar to those determined previously for different rhenium complexes with dimetal cores of the type syn-[Re$_2$(μ-O*R*)$_2$L$_2$(CO)$_6$] having bridging alkoxide or hydroxide ligands and terminal pyridine, dipyridyl and polypyridyl ligands (García-Vivó & Ruiz, 2020). The latter belong to a relatively large family of complexes which have been studied extensively because of their photophysical and chemical properties, host–guest interactions and biological activity.

After concluding that the crystal analyzed at the time, formed through crystallization from acetone/*n*-hexane of the bulk product obtained when reacting [Tc$_2$(CO)$_{10}$] with pyridine at room temperature, corresponds to the methoxide-bridged complex **syn-3** rather than the simple substitution product **syn-1**, the question then to be answered is from where could the methoxide ligands possibly arise. Unfortunately, we are not in a position to reproduce the above synthetic procedure in our laboratories, so we can only speculate about its possible origin. We currently trust that complex **syn-3** might just have been a very minor side product formed along with the major product, which just happened to crystallize first from the reaction mixture. Interestingly, we note that many dirhenium polypyridyl complexes with metal cores of the type syn-[Re$_2$(μ-O*R*)$_2$L$_2$(CO)$_6$] have been made by reacting [Re$_2$(CO)$_{10}$] with stoichiometric amounts of the pertinent N-donor ligand in the corresponding alcohol (*R*OH) or water, although high temperatures are typically required to form these products. However, a separate experiment carried out previously by us revealed that stirring [Re$_2$(CO)$_{10}$] in pyridine at room temperature for 4 d caused no detectable transformation on the Re$_2$ substrate, unless air is admitted into the reaction flask (García-Vivó & Ruiz, 2020). Based on the above indirect pieces of evidence, we tend now to think that formation of the methoxide-bridged complex **syn-3** during the slow reaction of [Tc$_2$(CO)$_{10}$] with pyridine at room temperature (5 d) might have followed from the presence of trace amounts of methanol and air in the reaction mixture.

4. Conclusion

The raw diffraction data of the compound formulated in 2008 as syn-[Tc$_2$(μ-CO)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] have now been re-processed under the hypothesis that the bridging ligands might actually be either hydroperoxide or methoxide ligands. The latter option proved to be the correct one, as it leads not only to better agreement parameters, such as *R*, *wR* or GOF, but also to chemically more sensible interatomic distances and displacement parameters for the non-H atoms of the bridging ligands. The formation of syn-[Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] in the room-temperature reaction of [Tc$_2$(CO)$_{10}$] with pyridine might have been facilitated at the time by the presence of unnoticed trace amounts of methanol and air in the reaction mixture.

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supporting information

X-ray-determined structure of the technetium complex [Tc$_2$(μ-CO)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] revisited: [Tc$_2$(μ-OMe)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] as the correct formulation

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Computing details

For both structures, program(s) used to solve structure: *SHELXL2017* (Sheldrick, 2015*b*) in *WinGX* (Farrugia, 2012); program(s) used to refine structure: SHELXT2014 (Sheldrick, 2015*a*); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

Di-μ-peroxido-bis[tricarbonyl(pyridine)technetium] *syn*-[Tc$_2$(CH$_3$O)$_2$(NC$_5$H$_5$)$_2$(CO)$_6$] (syn2)

Crystal data

[Tc$_2$(HO$_2$)$_2$(C$_5$H$_5$N)$_2$(CO)$_6$]	$F(000) = 1152$
$M_r = 588.28$	$D_x = 1.714$ Mg m^{-3}
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 18.116$ (16) Å	$\mu = 1.26$ mm^{-1}
$b = 10.359$ (8) Å	$T = 200$ K
$c = 12.148$ (10) Å	, colorless
$V = 2280$ (3) Å^3	$0.3 \times 0.2 \times 0.2$ mm
$Z = 4$	

Data collection

Siemens Nicolet Syntex R3m/V diffractometer	$\theta_{max} = 27.0°$, $\theta_{min} = 2.3°$
2614 measured reflections	$h = -19 \rightarrow 23$
2614 independent reflections	$k = -13 \rightarrow 8$
2265 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 2.8233P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.122$	$\Delta\rho_{max} = 1.12$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.97$ e Å^{-3}
2614 reflections	Extinction correction: SHELXL2014
281 parameters	(Sheldrick, 2015*b*),
4 restraints	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0030 (4)
Hydrogen site location: mixed	Absolute structure: No quotients, so Flack parameter determined by classical intensity fit
Only H-atom displacement parameters refined	Absolute structure parameter: 0.04 (9)

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}
Tc1	0.40833 (4)	0.80691 (7)	0.49957 (6)	0.0389 (2)
Tc2	0.29129 (3)	0.74681 (7)	0.70890 (8)	0.03599 (19)
O1	0.3474 (5)	1.0862 (7)	0.4879 (9)	0.072 (2)
O2	0.4001 (6)	0.8051 (10)	0.2445 (8)	0.076 (3)
O3	0.5616 (5)	0.9329 (10)	0.4740 (9)	0.075 (3)
O4B	0.4419 (6)	0.8844 (11)	0.7446 (9)	0.082 (3)
O5B	0.2428 (9)	0.7334 (16)	0.4609 (10)	0.116 (5)
O6	0.2295 (4)	1.0247 (7)	0.7043 (10)	0.069 (2)
O7	0.1264 (4)	0.6803 (10)	0.7349 (8)	0.071 (3)
O8	0.3006 (5)	0.7811 (12)	0.9603 (8)	0.078 (3)
N1	0.4528 (4)	0.6049 (7)	0.5105 (8)	0.0383 (16)
N2	0.3282 (4)	0.5403 (7)	0.7176 (7)	0.0372 (15)
C1	0.3693 (6)	0.9809 (10)	0.4936 (11)	0.053 (2)
C2	0.4032 (7)	0.8043 (15)	0.3418 (13)	0.061 (4)
C3	0.5047 (6)	0.8826 (10)	0.4845 (11)	0.055 (3)
O4	0.4056 (3)	0.7889 (7)	0.6774 (7)	0.0343 (17)
O5	0.3036 (4)	0.7139 (8)	0.5344 (6)	0.0374 (15)
C6	0.2552 (5)	0.9227 (10)	0.7038 (10)	0.047 (2)
C7	0.1898 (5)	0.7011 (12)	0.7244 (10)	0.052 (2)
C8	0.2977 (7)	0.7689 (14)	0.8681 (15)	0.061 (4)
C9	0.5176 (6)	0.5817 (10)	0.5665 (8)	0.046 (2)
H9	0.5417	0.6513	0.6024	0.066 (13)*
C10	0.5490 (6)	0.4571 (12)	0.5718 (10)	0.055 (3)
H10	0.5937	0.4430	0.6107	0.066 (13)*
C11	0.5134 (6)	0.3554 (11)	0.5192 (10)	0.056 (3)
H11	0.5338	0.2709	0.5215	0.066 (13)*
C12	0.4483 (6)	0.3780 (11)	0.4635 (9)	0.053 (3)
H12	0.4230	0.3096	0.4276	0.066 (13)*
C13	0.4199 (5)	0.5063 (9)	0.4610 (8)	0.043 (2)
H13	0.3753	0.5220	0.4220	0.066 (13)*
C14	0.3902 (6)	0.5067 (10)	0.7709 (9)	0.046 (2)
H14	0.4198	0.5725	0.8028	0.066 (13)*
C15	0.4128 (6)	0.3779 (12)	0.7809 (10)	0.055 (3)
H15	0.4567	0.3567	0.8197	0.066 (13)*
C16	0.3705 (7)	0.2823 (10)	0.7337 (10)	0.055 (3)
H16	0.3851	0.1945	0.7392	0.066 (13)*
C17	0.3064 (6)	0.3156 (10)	0.6779 (9)	0.049 (2)
H17	0.2762	0.2514	0.6448	0.066 (13)*
C18	0.2872 (5)	0.4471 (10)	0.6717 (8)	0.044 (2)

H18	0.2435	0.4707	0.6335	0.066 (13)*
H4B	0.46 (4)	0.96 (3)	0.72 (2)	1.4 (15)*
H5B	0.248 (7)	0.721 (12)	0.387 (3)	0.05 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tc1	0.0428 (3)	0.0385 (4)	0.0354 (3)	0.0053 (3)	0.0039 (4)	0.0030 (4)
Tc2	0.0338 (3)	0.0386 (4)	0.0356 (3)	0.0011 (3)	0.0005 (3)	−0.0025 (3)
O1	0.102 (6)	0.047 (4)	0.068 (5)	0.019 (4)	0.007 (5)	0.018 (5)
O2	0.101 (7)	0.087 (7)	0.040 (5)	0.013 (5)	−0.002 (4)	0.005 (4)
O3	0.058 (4)	0.076 (6)	0.092 (8)	−0.004 (4)	0.010 (5)	0.025 (6)
O4B	0.081 (6)	0.083 (7)	0.083 (7)	−0.007 (5)	−0.008 (5)	−0.010 (6)
O5B	0.107 (9)	0.183 (15)	0.058 (6)	−0.005 (9)	−0.027 (7)	−0.003 (7)
O6	0.063 (4)	0.046 (4)	0.098 (7)	0.016 (3)	0.012 (6)	−0.012 (5)
O7	0.038 (4)	0.104 (7)	0.070 (6)	−0.011 (4)	−0.001 (4)	0.002 (5)
O8	0.080 (6)	0.121 (8)	0.034 (4)	−0.013 (6)	0.006 (4)	−0.016 (5)
N1	0.041 (3)	0.037 (4)	0.037 (4)	0.003 (3)	0.003 (4)	0.004 (4)
N2	0.039 (3)	0.037 (4)	0.035 (4)	0.000 (3)	0.003 (3)	−0.002 (3)
C1	0.067 (6)	0.052 (5)	0.038 (5)	0.016 (4)	0.011 (6)	0.003 (5)
C2	0.062 (8)	0.083 (10)	0.039 (7)	0.004 (6)	0.000 (5)	0.003 (6)
C3	0.055 (5)	0.052 (6)	0.058 (7)	0.003 (5)	−0.001 (5)	0.019 (6)
O4	0.041 (4)	0.036 (3)	0.026 (4)	−0.004 (3)	0.000 (2)	−0.002 (3)
O5	0.034 (3)	0.050 (4)	0.028 (3)	−0.003 (3)	−0.009 (2)	0.001 (3)
C6	0.039 (4)	0.053 (5)	0.049 (5)	0.002 (4)	0.003 (5)	−0.017 (5)
C7	0.038 (5)	0.070 (6)	0.049 (6)	−0.001 (4)	0.006 (4)	−0.010 (6)
C8	0.064 (8)	0.058 (7)	0.060 (10)	−0.018 (6)	0.004 (6)	−0.008 (6)
C9	0.048 (5)	0.050 (5)	0.042 (5)	0.005 (4)	−0.004 (4)	−0.002 (4)
C10	0.049 (5)	0.059 (7)	0.057 (6)	0.011 (5)	0.006 (5)	0.004 (5)
C11	0.063 (6)	0.045 (5)	0.059 (8)	0.015 (5)	0.015 (5)	0.007 (5)
C12	0.063 (6)	0.044 (5)	0.051 (6)	0.005 (5)	0.004 (5)	−0.010 (5)
C13	0.050 (5)	0.034 (4)	0.047 (5)	−0.001 (4)	−0.004 (4)	−0.004 (4)
C14	0.054 (5)	0.040 (5)	0.043 (5)	0.004 (4)	−0.010 (4)	−0.002 (4)
C15	0.060 (6)	0.057 (6)	0.049 (6)	0.014 (5)	−0.007 (5)	0.004 (5)
C16	0.074 (7)	0.039 (5)	0.052 (7)	0.012 (5)	0.005 (5)	0.008 (4)
C17	0.057 (6)	0.037 (5)	0.053 (6)	−0.010 (4)	−0.006 (4)	0.004 (4)
C18	0.047 (5)	0.045 (5)	0.041 (5)	−0.008 (4)	−0.004 (4)	−0.002 (4)

Geometric parameters (Å, º)

Tc1—N1	2.246 (7)	O5B—O5	1.433 (14)
Tc1—C1	1.937 (10)	O6—C6	1.155 (12)
Tc1—C2	1.919 (16)	O7—C7	1.176 (12)
Tc1—C3	1.922 (11)	O8—C8	1.13 (2)
Tc1—O4	2.168 (9)	N1—C9	1.377 (12)
Tc1—O5	2.170 (7)	N1—C13	1.327 (12)
Tc2—N2	2.244 (7)	N2—C14	1.342 (12)
Tc2—O4	2.150 (7)	N2—C18	1.339 (12)

Tc2—O5	2.158 (8)	C9—C10	1.412 (15)
Tc2—C6	1.937 (10)	C10—C11	1.391 (17)
Tc2—C7	1.907 (10)	C11—C12	1.380 (16)
Tc2—C8	1.951 (18)	C12—C13	1.426 (14)
O1—C1	1.162 (12)	C14—C15	1.401 (15)
O2—C2	1.183 (19)	C15—C16	1.376 (17)
O3—C3	1.162 (14)	C16—C17	1.389 (16)
O4B—O4	1.441 (12)	C17—C18	1.408 (14)
C1—Tc1—N1	178.7 (4)	C8—Tc2—O5	170.4 (4)
C1—Tc1—O4	96.3 (4)	C9—N1—Tc1	119.8 (6)
C1—Tc1—O5	95.8 (4)	C13—N1—Tc1	121.9 (6)
C2—Tc1—N1	93.6 (5)	C13—N1—C9	118.2 (8)
C2—Tc1—C1	87.6 (6)	C14—N2—Tc2	121.3 (6)
C2—Tc1—C3	87.4 (6)	C18—N2—Tc2	120.1 (6)
C2—Tc1—O4	173.0 (4)	C18—N2—C14	118.5 (8)
C2—Tc1—O5	98.4 (5)	O1—C1—Tc1	178.1 (10)
C3—Tc1—N1	93.4 (4)	O2—C2—Tc1	178.8 (14)
C3—Tc1—C1	87.1 (5)	O3—C3—Tc1	177.3 (10)
C3—Tc1—O4	98.7 (4)	Tc2—O4—Tc1	102.5 (3)
C3—Tc1—O5	173.6 (4)	O4B—O4—Tc1	119.6 (7)
O4—Tc1—N1	82.5 (3)	O4B—O4—Tc2	118.6 (6)
O4—Tc1—O5	75.4 (3)	Tc2—O5—Tc1	102.2 (3)
O5—Tc1—N1	83.6 (3)	O5B—O5—Tc1	119.3 (8)
O4—Tc2—N2	85.1 (3)	O5B—O5—Tc2	120.7 (8)
O4—Tc2—O5	76.0 (3)	O6—C6—Tc2	175.4 (9)
O5—Tc2—N2	82.2 (3)	O7—C7—Tc2	176.2 (11)
C6—Tc2—N2	177.5 (3)	O8—C8—Tc2	179.2 (13)
C6—Tc2—O4	97.4 (3)	N1—C9—C10	121.7 (10)
C6—Tc2—O5	98.8 (4)	C11—C10—C9	119.0 (10)
C6—Tc2—C8	86.6 (6)	C12—C11—C10	119.5 (10)
C7—Tc2—N2	92.6 (4)	C11—C12—C13	118.6 (10)
C7—Tc2—O4	174.8 (4)	N1—C13—C12	123.0 (9)
C7—Tc2—O5	99.1 (4)	N2—C14—C15	122.2 (10)
C7—Tc2—C6	84.9 (4)	C16—C15—C14	119.1 (10)
C7—Tc2—C8	89.3 (5)	C15—C16—C17	119.4 (10)
C8—Tc2—N2	92.7 (5)	C16—C17—C18	118.2 (9)
C8—Tc2—O4	95.5 (5)	N2—C18—C17	122.6 (9)

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di-μ-methoxido-bis[tricarbonyl(pyridine)technetium], *syn*-[Tc₂(CH₃O)₂(NC₅H₅)₂(CO)₆] (syn3)

Crystal data
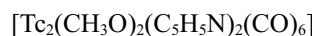
[Tc₂(CH₃O)₂(C₅H₅N)₂(CO)₆]	$V = 2280\ (3)$ Å³
$M_r = 584.33$	$Z = 4$
Orthorhombic, $Pna2_1$	$F(000) = 1152$
$a = 18.116\ (16)$ Å	$D_x = 1.702$ Mg m⁻³
$b = 10.359\ (8)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 12.148\ (10)$ Å	$\mu = 1.26$ mm⁻¹

$T = 200$ K	$0.3 \times 0.2 \times 0.2$ mm
, colorless	

Data collection

Siemens Nicolet Syntex R3m/V diffractometer	$\theta_{max} = 27.0°$, $\theta_{min} = 2.3°$
	$h = -19 \rightarrow 23$
2614 measured reflections	$k = -13 \rightarrow 8$
2614 independent reflections	$l = -10 \rightarrow 15$
2265 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 2.1707P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.113$	$\Delta\rho_{max} = 1.13$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -1.03$ e Å^{-3}
2614 reflections	Extinction correction: SHELXL2014
274 parameters	(Sheldrick, 2015*b*),
1 restraint	$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0027 (4)
Hydrogen site location: inferred from neighbouring sites	Absolute structure: No quotients, so Flack parameter determined by classical intensity fit
H-atom parameters constrained	Absolute structure parameter: 0.02 (8)

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}
O1	0.3474 (5)	1.0858 (7)	0.4880 (8)	0.073 (2)
O2	0.4008 (5)	0.8066 (10)	0.2443 (7)	0.078 (3)
O3	0.5615 (4)	0.9325 (9)	0.4743 (9)	0.077 (3)
O4	0.4059 (3)	0.7895 (7)	0.6772 (6)	0.0346 (16)
O5	0.3036 (4)	0.7137 (7)	0.5342 (6)	0.0379 (14)
O6	0.2294 (4)	1.0246 (7)	0.7049 (9)	0.070 (2)
O7	0.1264 (4)	0.6800 (9)	0.7355 (8)	0.071 (2)
O8	0.2997 (5)	0.7804 (11)	0.9605 (7)	0.078 (3)
N1	0.4529 (3)	0.6053 (7)	0.5102 (7)	0.0379 (15)
N2	0.3279 (3)	0.5405 (6)	0.7179 (6)	0.0370 (14)
C1	0.3690 (5)	0.9810 (9)	0.4936 (10)	0.053 (2)
C2	0.4030 (7)	0.8046 (14)	0.3420 (12)	0.063 (4)
C3	0.5048 (6)	0.8829 (10)	0.4843 (10)	0.056 (3)
C4	0.4421 (5)	0.8837 (9)	0.7433 (8)	0.044 (2)
H4A	0.4176	0.9674	0.7342	0.066*
H4B	0.4938	0.8910	0.7203	0.066*
H4C	0.4399	0.8576	0.8207	0.066*
C5	0.2435 (6)	0.7327 (13)	0.4615 (9)	0.061 (3)

H5A	0.2019	0.6787	0.4846	0.091*	
H5B	0.2584	0.7089	0.3866	0.091*	
H5C	0.2287	0.8237	0.4628	0.091*	
C6	0.2553 (4)	0.9227 (9)	0.7041 (10)	0.048 (2)	
C7	0.1901 (5)	0.7010 (11)	0.7240 (9)	0.053 (2)	
C8	0.2970 (7)	0.7691 (13)	0.8678 (14)	0.058 (4)	
C9	0.5175 (5)	0.5815 (9)	0.5663 (8)	0.046 (2)	
H9	0.5417	0.6510	0.6024	0.055*	
C10	0.5489 (5)	0.4568 (11)	0.5718 (9)	0.055 (2)	
H10	0.5935	0.4426	0.6111	0.066*	
C11	0.5134 (6)	0.3554 (10)	0.5189 (9)	0.057 (3)	
H11	0.5339	0.2710	0.5208	0.068*	
C12	0.4482 (6)	0.3784 (10)	0.4636 (9)	0.054 (2)	
H12	0.4227	0.3099	0.4281	0.065*	
C13	0.4197 (5)	0.5062 (9)	0.4607 (8)	0.044 (2)	
H13	0.3751	0.5217	0.4217	0.053*	
C14	0.3900 (5)	0.5067 (9)	0.7710 (8)	0.046 (2)	
H14	0.4195	0.5724	0.8033	0.055*	
C15	0.4127 (6)	0.3789 (11)	0.7806 (9)	0.053 (2)	
H15	0.4566	0.3582	0.8193	0.064*	
C16	0.3709 (6)	0.2825 (9)	0.7333 (9)	0.054 (3)	
H16	0.3858	0.1948	0.7386	0.065*	
C17	0.3063 (5)	0.3156 (9)	0.6776 (8)	0.049 (2)	
H17	0.2761	0.2514	0.6447	0.059*	
C18	0.2873 (5)	0.4469 (9)	0.6718 (8)	0.045 (2)	
H18	0.2437	0.4704	0.6334	0.053*	
Tc1	0.40832 (3)	0.80689 (6)	0.49960 (6)	0.03886 (19)	
Tc2	0.29129 (3)	0.74678 (7)	0.70886 (8)	0.03592 (17)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.103 (5)	0.047 (4)	0.068 (5)	0.019 (4)	0.007 (5)	0.019 (4)
O2	0.104 (7)	0.091 (7)	0.039 (4)	0.020 (5)	0.000 (4)	0.005 (4)
O3	0.058 (4)	0.078 (5)	0.095 (8)	−0.004 (4)	0.009 (5)	0.028 (5)
O4	0.041 (4)	0.036 (3)	0.028 (3)	−0.003 (2)	0.000 (2)	−0.003 (2)
O5	0.038 (3)	0.048 (3)	0.028 (3)	−0.001 (3)	−0.010 (2)	0.001 (3)
O6	0.064 (4)	0.045 (4)	0.101 (6)	0.016 (3)	0.009 (5)	−0.010 (5)
O7	0.039 (3)	0.102 (6)	0.072 (6)	−0.009 (4)	−0.001 (4)	0.003 (5)
O8	0.082 (6)	0.119 (8)	0.034 (4)	−0.012 (5)	0.006 (4)	−0.017 (4)
N1	0.041 (3)	0.036 (3)	0.036 (4)	0.003 (2)	0.003 (3)	0.004 (3)
N2	0.039 (3)	0.038 (3)	0.034 (3)	−0.001 (3)	0.003 (3)	−0.002 (3)
C1	0.069 (6)	0.051 (5)	0.038 (4)	0.015 (4)	0.014 (6)	0.001 (5)
C2	0.065 (8)	0.085 (10)	0.039 (7)	0.004 (6)	−0.001 (5)	0.005 (5)
C3	0.058 (5)	0.055 (5)	0.054 (6)	0.001 (4)	−0.003 (5)	0.019 (5)
C4	0.039 (4)	0.046 (5)	0.048 (5)	−0.002 (4)	−0.001 (4)	−0.005 (4)
C5	0.045 (5)	0.092 (8)	0.045 (5)	0.000 (5)	−0.013 (4)	0.000 (5)
C6	0.039 (4)	0.052 (5)	0.052 (5)	0.002 (4)	0.002 (4)	−0.017 (5)

C7	0.040 (4)	0.069 (6)	0.050 (6)	−0.002 (4)	0.005 (4)	−0.008 (5)
C8	0.059 (7)	0.055 (6)	0.060 (9)	−0.014 (5)	0.005 (5)	−0.010 (6)
C9	0.046 (5)	0.050 (5)	0.042 (5)	0.006 (4)	−0.004 (4)	−0.004 (4)
C10	0.048 (5)	0.061 (6)	0.056 (6)	0.010 (4)	0.005 (4)	0.003 (5)
C11	0.062 (5)	0.046 (5)	0.063 (8)	0.014 (4)	0.015 (5)	0.007 (5)
C12	0.065 (6)	0.044 (5)	0.053 (6)	0.002 (5)	0.003 (5)	−0.010 (4)
C13	0.046 (5)	0.037 (4)	0.048 (5)	−0.002 (4)	−0.003 (4)	−0.006 (4)
C14	0.054 (5)	0.042 (5)	0.043 (5)	0.002 (4)	−0.010 (4)	−0.001 (4)
C15	0.054 (5)	0.055 (6)	0.051 (5)	0.011 (4)	−0.010 (4)	0.003 (5)
C16	0.071 (6)	0.039 (5)	0.053 (6)	0.014 (4)	0.005 (5)	0.007 (4)
C17	0.059 (5)	0.038 (4)	0.050 (5)	−0.008 (4)	−0.007 (4)	0.003 (4)
C18	0.049 (5)	0.044 (5)	0.041 (4)	−0.008 (4)	−0.005 (4)	−0.002 (4)
Tc1	0.0428 (3)	0.0385 (3)	0.0353 (3)	0.0053 (3)	0.0039 (4)	0.0030 (4)
Tc2	0.0336 (3)	0.0386 (3)	0.0355 (3)	0.0011 (3)	0.0005 (3)	−0.0025 (3)

Geometric parameters (Å, º)

O1—C1	1.157 (11)	N2—C18	1.339 (11)
O2—C2	1.187 (18)	N2—Tc2	2.240 (7)
O3—C3	1.155 (13)	C1—Tc1	1.940 (9)
O4—C4	1.424 (11)	C2—Tc1	1.917 (15)
O4—Tc1	2.166 (8)	C3—Tc1	1.926 (11)
O4—Tc2	2.157 (6)	C6—Tc2	1.936 (9)
O5—C5	1.415 (11)	C7—Tc2	1.903 (9)
O5—Tc1	2.170 (7)	C8—Tc2	1.947 (16)
O5—Tc2	2.160 (8)	C9—C10	1.413 (14)
O6—C6	1.155 (11)	C10—C11	1.389 (16)
O7—C7	1.183 (11)	C11—C12	1.380 (15)
O8—C8	1.134 (18)	C12—C13	1.421 (14)
N1—C9	1.376 (11)	C14—C15	1.391 (14)
N1—C13	1.333 (11)	C15—C16	1.378 (16)
N1—Tc1	2.243 (7)	C16—C17	1.393 (15)
N2—C14	1.343 (11)	C17—C18	1.405 (13)
C4—O4—Tc1	119.7 (6)	O4—Tc1—N1	82.7 (3)
C4—O4—Tc2	119.0 (6)	O5—Tc1—N1	83.7 (3)
Tc2—O4—Tc1	102.4 (3)	C1—Tc1—O4	96.1 (4)
C5—O5—Tc1	119.3 (7)	C1—Tc1—O5	95.7 (4)
C5—O5—Tc2	120.8 (7)	C1—Tc1—N1	178.8 (4)
Tc2—O5—Tc1	102.1 (3)	C2—Tc1—O4	173.2 (4)
C9—N1—Tc1	120.1 (6)	C2—Tc1—O5	98.3 (5)
C13—N1—C9	118.0 (8)	C2—Tc1—N1	93.6 (5)
C13—N1—Tc1	121.9 (6)	C2—Tc1—C1	87.5 (6)
C14—N2—Tc2	121.4 (6)	C2—Tc1—C3	87.4 (5)
C18—N2—C14	118.1 (8)	C3—Tc1—O4	98.6 (4)
C18—N2—Tc2	120.5 (6)	C3—Tc1—O5	173.8 (4)
O1—C1—Tc1	177.9 (9)	C3—Tc1—N1	93.4 (3)
O2—C2—Tc1	178.1 (13)	C3—Tc1—C1	87.1 (4)

O3—C3—Tc1	177.6 (9)	O4—Tc2—O5	76.0 (3)
O6—C6—Tc2	175.2 (9)	O4—Tc2—N2	85.4 (2)
O7—C7—Tc2	176.0 (10)	O5—Tc2—N2	82.3 (3)
O8—C8—Tc2	179.0 (13)	C6—Tc2—O4	97.2 (3)
N1—C9—C10	121.9 (9)	C6—Tc2—O5	98.9 (4)
C11—C10—C9	118.9 (9)	C6—Tc2—N2	177.3 (3)
C12—C11—C10	119.4 (9)	C6—Tc2—C8	86.3 (5)
C11—C12—C13	118.9 (9)	C7—Tc2—O4	174.7 (4)
N1—C13—C12	122.9 (9)	C7—Tc2—O5	98.9 (4)
N2—C14—C15	122.4 (9)	C7—Tc2—N2	92.4 (4)
C16—C15—C14	119.5 (9)	C7—Tc2—C6	85.0 (4)
C15—C16—C17	119.0 (9)	C7—Tc2—C8	89.1 (5)
C16—C17—C18	117.9 (9)	C8—Tc2—O4	95.8 (4)
N2—C18—C17	123.0 (8)	C8—Tc2—O5	170.8 (4)
O4—Tc1—O5	75.6 (2)	C8—Tc2—N2	92.8 (4)