X-ray Structure, Magnetic and Catalytic Properties of a Cyclic Trinuclear Co^{II}/Co^{III}/Co^{III} Complex with a μ^3-Hydroxy Anion

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The mixed-valent cyclic trinuclear cobalt(II)/cobalt(III)/cobalt(III) complex tris(dibenzoylmethanato-$1\kappa^2O,O';2\kappa^2O,O';3\kappa^2O,O'$)($\mu_3$-hydroxo-$1{:}2\kappa^2O;1{:}3\kappa^2O;2{:}3\kappa^2O$)tetrakis(μ-pyrazolato-$1{:}2\kappa^4N^1N^2;1{:}3\kappa^2N^1N^2;2{:}3\kappa^2N^1N^2$)-1,2-dicobalt(III)-3-cobalt(II) with four bridging pyrazolate anions and a μ^3-hydroxy anion has been synthesized and its molecular structure has been elucidated on the basis of X-ray crystallographic, magnetic, NMR, and EPR studies. The remaining coordination sites of the pentacoordinate cobalt(II) and hexacoordinate cobalt(III) centers are occupied by oxygen donor atoms of dibenzoylmethanate anions, rendering the complex soluble in most organic solvents. The complex has been found to effectively catalyze the decomposition of *tert*-butyl hydroperoxide (TBHP) in chlorobenzene with a short induction period and a half-life of 80 min and to catalyze the oxidation of cyclohexene to 2-cyclohexen-1-one with oxygen and to 2-cyclohexen-1-ol with TBHP.

Introduction

Multinuclear complexes of transition metal ions attract a lot of attention due to their potential catalytic activity. They are constructed using many different polydentate ligands including oxygen donor anionic ligands such as carboxylates[1−8] and other oxy anions.[9,10] Nitrogen-donor bridging ligands, especially pyrazoles, which are well-suited for N,N-bridging, are frequently utilized in the construction of such systems.[11−16] Amongst polynuclear systems, cyclic trinuclear complexes constitute an important class of compounds.[1−10,14−17] Cyclic trinuclear cobalt complexes have been found to show some catalytic activity in the epoxidation of olefins[1,18] and in the autoxidation of hydrocarbons.[19] Therefore, we have focused on the synthesis, isolation, and structural characterization of another, mixed-valent trinuclear cobalt complex soluble in organic solvents. The ligands used in the synthesis were dibenzoylmethanate (DBM) and pyrazolate (pz) anions. Starting from cobalt(II) nitrate, the synthetic procedure led to the isolation of a trinuclear cyclic Co^{III}/Co^{III}/Co^{II} complex, which has been characterized in the solid state by X-ray diffraction analysis. The product has been tested for its catalytic activity in the oxidation of hydrocarbons.

Results and Discussion

Synthetic Procedure and Analytical Data

The optimized synthetic route for obtaining a compound of the analytical formula $Co_3(DBM)_3(pz)_4(OH)\cdot 2THF$ (**1**·2THF) required the use of dibenzoylmethane (DBMH) and pyrazole (pzH) in a 4:3 stoichiometry and excess cobalt(II) salt under basic aerobic conditions. The yield was reasonable considering that a mixture of complexes was formed. The trinuclear complex **1**·2THF could be isolated as a pure compound by extraction into an organic solvent. Special care had to be taken due to the reactivity of **1** towards chlorinated hydrocarbons (vide infra). Brick-red crystals of **1**·2THF, which proved to be stable and analytically pure, were grown by crystallization from THF/hexane.

X-ray Crystallographic Results for the Cyclic Trinuclear Complex $Co_3(DBM)_3(pz)_4(OH)\cdot 2THF$

The molecular structure of **1**·2THF together with bond lengths and angles are presented in Figure 1. The core of the cyclic trinuclear complex **1** consists of three cobalt centers, pentacoordinate Co(1) and hexacoordinate Co(2) and Co(3) (for the numbering, see Figure 2). These are N,N-bridged by four pyrazolate anionic ligands, two of which bridge two cobalt ions, and are further bridged by a μ^3-hydroxide anion. The latter is displaced from the Co(1)-Co(2)Co(3) plane (P) by 0.441(1) Å. Three of the four bridging pyrazolate anions, i.e. pz$_{1a}$, pz$_{1b}$, and pz$_{2a}$, lie at the opposite side of the P plane in relation to μ$_3$-OH (i.e. in the *exo* position) and the angles between the pyrazolate ring planes and P are 38.5(1)°, 41.4(1)°, and 30.4(1)°, respectively. The fourth bridging pyrazolate, namely pz$_{2a}$, is *endo* with a pz$_{2a}$ vs. P angle of 67.8(1)°. The three DBM ligands are each involved in O,O-chelation of the cobalt centers. The chelate ring planes of the DBM ligands are twisted in relation to the P plane by about 86.7(1)° (DBM$_1$ vs. P), 61.5(1)° (DBM$_2$ vs. P), and 68.4(1)° (DBM$_3$ vs. P). Consequently, the oxygen donors and phenyl groups of the DBM ligands are non-equivalent, as reflected in the dis-

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tances of the oxygen atom donors from the P plane (see Figure 2). Three of the oxygen donors, i.e. O(2), O(3), and O(6), are *endo*, while O(1), O(4), and O(5) are *exo*. Thus, two sides of the molecule of **1** are different; the *endo* one is occupied by μ_3-OH, pz_{2a}, and mainly by DBM ligands, while the three remaining pyrazolate anions (*exo*) lie at the opposite side of the P plane. The cobalt centers are distinguished not only by their coordination numbers, but also in terms of the cobalt−donor atom distances. The bond lengths between the pentacoordinate Co(1) atom and both the bridging pyrazolate nitrogens and the DBM oxygen atoms are about 2.00 Å, whereas those between Co(2) and Co(3) and the corresponding pyrazolate nitrogen atoms and DBM oxygen atoms are 1.91 Å (Co−N averaged) and 1.89 Å (Co−O averaged), respectively. Furthermore, the bond lengths between the bridging hydroxy oxygen atom and Co(2) and Co(3) (1.91 Å) are shorter as compared to that between Co(1) and O(1B) (2.15 Å), which results in a lower value of Co(2)−O(1B)−Co(3) (108.6°) in comparison with the mean Co(1)−O(1B)−Co(*n*) angle (118.5°). It is also noteworthy that the pyrazolate anion pz_{2a} that bridges the Co(2) and Co(3) centers, i.e. the only *endo* pz, is the most strongly bound to the cobalt ions (1.89 Å) of all the bridging pyrazolate anions; the bond lengths between the pz_{2b} (*exo*) nitrogen atoms and the cobalt ions are longer (1.91 Å), and those between the pz_1 (*exo*) nitrogen atoms and the cobalt centers are longer still (1.92 Å). These structural features clearly demonstrate that the oxidation state of Co(1) is close to Co^{II}, whereas those of Co(2) and Co(3) centers are formally Co^{III}.[20] Analysis of the periphery of **1** revealed different conformations for the three DBM ligands; the phenyl rings at DBM_2 are almost coplanar with its chelate ring, while the *exo*-phenyl rings of the other two DBM ligands are twisted in relation to their chelate rings, presumably due to weak interactions between their *meta*-protons and the face of the *exo*-phenyl of DBM_1 (the contact distance is 2.78 Å, see Figure 1). However, the crystal puckering, including the interaction of **1** with two THF solvate molecules, may also affect the conformations of the DBM ligands.

Electronic Structure of 1

A rather unusual feature of **1** is that both a well-resolved ^1H NMR spectrum and an ESR spectrum (at liquid nitrogen temperature) could be obtained. Therefore, we have measured the magnetic susceptibility of **1**·2THF. The magnetic moment of **1**·2THF is indicative of a total spin of 3/2 and is slightly temperature-dependent (Figure 3, A). At 77 K, **1** gives a rhombic EPR spectrum with $g_1 = 5.35$, $g_2 = 3.34$, and $g_3 = 2.31$ (Figure 3, B). The extent of the delocalization of the unpaired electron could be estimated by ^1H NMR spectral studies of the high-spin complex **1**.

The spectrum consists of 22 resonances, which are partially overlapped (Figure 3, C). Although a total assignment could not be made, the two most shifted resonances, appearing at $\delta = 57$ and -59 with relative intensities of 2:1, could be attributed to 3,5-H and 4-H of one of the bridging pyrazolates (pz_2). The large number of resonances seen for **1** indicates that the asymmetry observed in the solid state is retained in solution, leading to a separation of the *o*-, *m*-, and *p*-H phenyl resonances of all three DBM ligands. On the other hand, the rotation of the phenyl groups within each DBM remains fast on the NMR time scale. Consequently, twelve resonances due to the DBM phenyl

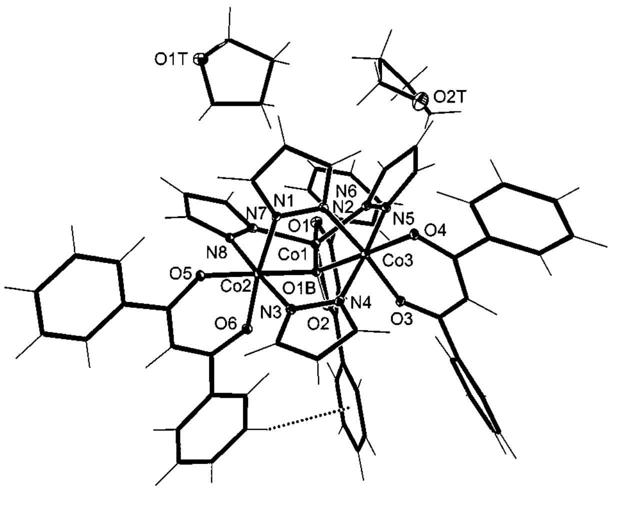

Figure 1. Projection[27] of the trinuclear cobalt complex; thermal ellipsoids are drawn at a 30% probability level; selected bond lengths [Å] and angles [°]: Co(1)−N(7) 1.991(2), Co(1)−N(6) 2.002(2), Co(1)−O(1) 2.014(2), Co(1)−O(2) 1.981(2), Co(1)−O(1B) 2.154(2), Co(2)−N(1) 1.886(2), Co(2)−N(3) 1.900(2), Co(2)−N(8) 1.920(2), Co(2)−O(5) 1.879(2), Co(2)−O(6) 1.881(2), Co(2)−O(1B) 1.912(2), Co(3)−N(2) 1.892(2), Co(3)−N(4) 1.917(2), Co(3)−N(5) 1.926(2), Co(3)−O(3) 1.898(2), Co(3)−O(4) 1.886(2), Co(3)−O(1B) 1.914(2); Co(2)−O(1B)−Co(3) 108.58(8), Co(2)−O(1B)−Co(1) 117.77(8), Co(3)−O(1B)−Co(1) 119.32(8); the ellipsoids at carbon atom positions and most of the atom labels are omitted for clarity; the contact between the *meta*-hydrogen atom of the *endo*-phenyl ring of DBM_2 and the face of the *endo*-phenyl ring of DBM_1 are shown with a dotted line (for acronyms used, see Figure 2)

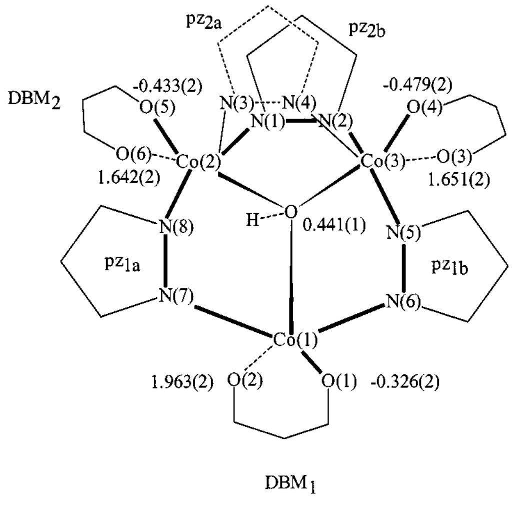

Figure 2. Simplified representation of **1** showing selected donor atoms and acronyms used throughout the discussion; the distances between the oxygen donor atoms of the DBM ligands and the mean Co(1)Co(2)Co(3) plane [Å] are indicated in the scheme; positive values are attributed to the *endo* side; bridging pyrazolates pz_{1a}, pz_{1b}, and pz_{2b} are bound at the *exo* side

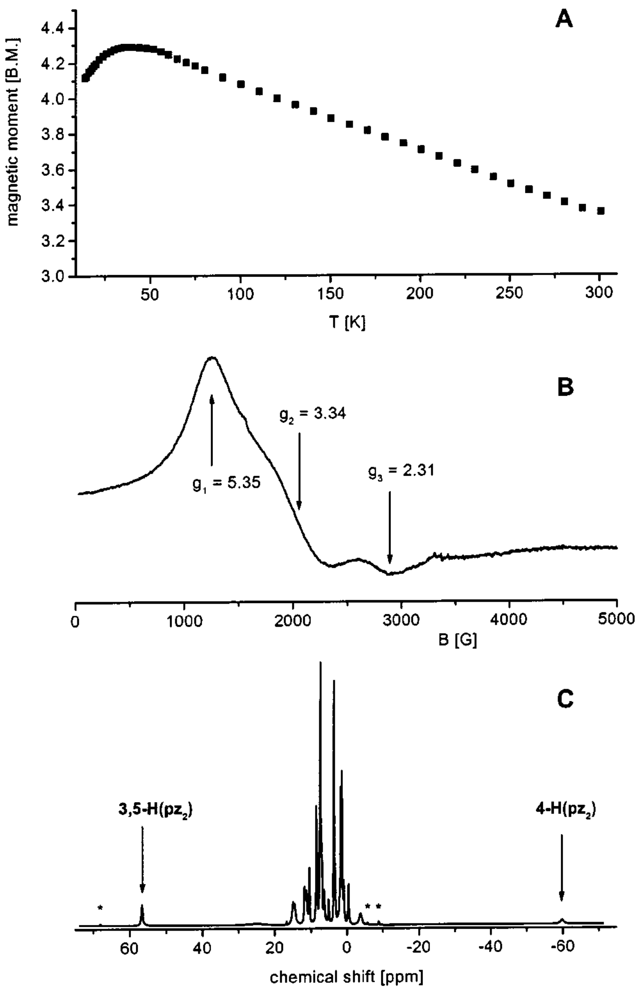

Figure 3. A: temperature dependence of the magnetic moment; B: ESR spectrum measured in toluene glass at 77 K; C: ^{1}H NMR spectrum of **1** in $CDCl_3$ at 293 K; the resonances due to the product of conversion of **1** are labeled with asterisks

groups, two resonances due to the C−H of DBM, the resonance of the central OH, three pz_1 signals, and four pz_2 signals give a total of 22 resonances for **1**. The well-resolved ^{1}H NMR spectrum of **1** is consistent with a high-spin configuration of the Co^{II} center and indicates rather extensive delocalization of the unpaired electron over the formally $Co^{II}/Co^{III}/Co^{III}$ core.

Complex **1** was found to be unstable in chlorinated solvents (chloroform and dichloromethane). Presumably, chloride ions are abstracted from the solvent through formation of a new complex **1′**; the half-life for this conversion was estimated to be ca. 24 h. The spectrum of **1′** is present even in a freshly prepared solution (Figure 3, C). Complex **1′** becomes predominant in a synthetic mixture if removal of CH_2Cl_2 is delayed. In the case of the analogous complex with acetylacetonate (acac) instead of DBM, the instability of the trinuclear OH-bridged complex is even greater and the only product isolated was $Co_3(acac)_3(pz)_4Cl$. We have attempted to replace the DBM in **1** with benzoylacetonate anions; the product thus obtained was found to be a mixture of complexes due to the additional asymmetry introduced by this β-diketonate, resulting in a multiplication of the 3(5)-H and 4-H (pz_2) resonances, although the chemical shift of the latter was very close to that in **1**. This observation confirmed the assignment of the ^{1}H NMR resonances of **1** on the basis of its symmetry and that of its analogues with other β-diketonate anions.

Catalytic Properties

Complex **1** has been found to catalyze the decomposition of *tert*-butyl hydroperoxide (TBHP) in chlorobenzene with a short induction period and a half-life of 80 min. We have tested **1** for its catalytic ability in the oxidation of cyclohexene by TBHP and dioxygen. These two oxidants showed different chemoselectivities; in the former case active oxygen was selectively transferred to the substrate with formation of 2-cyclohexen-1-ol, while in all other cases 2-cyclohexen-1-one was the dominant product (Table 1).

Generation of the active form of the catalyst from **1** in acetonitrile required a long induction period (Entry 3), whereas a short induction period was observed in chlorobenzene. This induction period is consistent with the building-up of an appropriately high concentration of ROOH from R (alkene, alkane) and O_2. Addition of TBHP to the reaction mixtures (Entry 4) obviated the need for such an induction period. The main products clearly showed the involvement of different catalytic forms of **1**, although both are the common products of oxygenated Fenton chemistry.[22−24] Generally, oxidation of organic substrates catalyzed by cobalt complexes can be divided into two categories based on the type of mechanism involved: free-radical autoxidation and catalytic oxygen transfer.[22] In the first type of reaction, the cobalt catalyst induces decomposition of an organic hydroperoxide (ROOH) to form radicals according to a Haber−Weiss mechanism. However, the primary chemistry of ROOH towards metal coordination complexes is nucleophilic addition and ligand substitution with formation of the reactive intermediate for Fenton chemistry and the precursor to the reactive intermediate for oxygenated Fenton chemistry (in the presence of O_2).[23] Catalytic oxygen transfer involves two major active species, namely the peroxometal and oxometal complexes, as the active oxidants.[24] The product derived from **1** in the presence of dioxygen led to the oxidation of cumene in a similar reaction. The products obtained were found to be those derived from attack of the active form of **1** on the secondary carbon atoms (cumene and ethylbenzene, Entries 5 and 7) and not the primary carbon atoms (*p*-xylene, Entry 6) of aliphatic substrates.

Although the catalytic activity and chemoselectivity of **1** are relatively low, we are currently modifying the trinuclear cyclic complexes by replacing DBM with unsymmetrical β-diketonates and by replacing the cobalt ions with other metal ions with a view to improving the catalytic activity of these systems.

Table 1. The results of tests of the catalytic ability of tris(dibenzoylmethanato-1κ^2O,O';2κ^2O,O';3κ^2O,O')(μ_3-hydroxo-1:2κ^2O;1:3κ^2O;2:3κ^2O)tetrakis(μ-pyrazolato-1:2$\kappa^4N^1N^2$;1:3$\kappa^2N^1N^2$;2:3$\kappa^2N^1N^2$)-1,2-dicobalt(III)-3-cobalt(II) (**1**)

Test[a]	Substrate (concentration)	Solvent	Oxidant	$\tau_{1/2}$ [min]	Products; yields [%][b]
1	cyclohexene (2.1 м)	chlorobenzene	TBHP (0.276 м)	120	2-cyclohexen-1-ol; 65.4 2-cyclohexen-1-one; 6.4 cyclohexane-1,2-epoxide; 3.2 total yield 75.0 (24 h)
2	cyclohexene (0.97 м)	chlorobenzene	O_2 (1 atm)	120[c]	2-cyclohexen-1-ol; 21.1 2-cyclohexen-1-one; 49.1 cyclohexane-1,2-epoxide; 7.3 total yield 77.4 (18.5 h)
3	cyclohexene (0.97 м)	acetonitrile	O_2 (1 atm)	450[c]	2-cyclohexen-1-ol; 6.4 2-cyclohexen-1-one; 44.8 cyclohexane-1,2-epoxide; 9.9 Total yield 61.4 (20 h)
4	cyclohexene (0.97 м)	acetonitrile	O_2 (1 atm) + TBHP[e]	150	2-cyclohexen-1-ol; 13.1 2-cyclohexen-1-one; 48.8 cyclohexane-1,2-epoxide; 1.0 Total yield 68.1 (18.5 h)
5	cumene (1.0 м)	chlorobenzene	O_2 (1 atm)	600	2-phenylpropan-2-ol; 11.5 acetophenone; 10.8 cumene hydroperoxide; 3.6 Total yield 25.8 (20 h)
6	*p*-xylene (0.98 м)	chlorobenzene	O_2 (1 atm)	[d]	no conversion products were found (20 h)
7	ethylbenzene (0.98 м)	chlorobenzene	O_2 (1 atm)	600	acetophenone; 6.1 (18.5 h)

[a] The concentration of **1** was $5\cdot10^{-4}$ mol/dm^3. − [b] Calculated on the basis of substrate consumed, except for Entry 1, where the yield was calculated on the basis of active oxygen transferred to the organic substrate. − [c] With an induction period of 30 min (Entry 2) and 300 min (Entry 3); $\tau_{1/2}$ calculated starting from the point at which consumption of oxygen commenced. − [d] No consumption of oxygen was noticed. − [e] The initial concentration of TBHP was $1.5\cdot10^{-4}$ м.

Experimental Section

Synthesis: In the optimized procedure, dibenzoylmethane (DBMH, 500 mg, 2.232 mmol) and pyrazole (pzH, 202 mg, 2.976 mmol) were dissolved in tetrahydrofuran (THF, 20 mL) and the resulting solution was added dropwise to a 0.3 mol·dm^{-3} aq. cobalt(II) nitrate solution (75 mL) under vigorous stirring. Then, freshly distilled dichloromethane (150 mL) was added to the mixture to extract the desired, non-electrolyte product into the organic phase. Additionally, 1 м aq. NaOH was added dropwise to the mixture under continuous stirring. After stirring for a further 10 min, the reddish-brown organic phase was collected and the CH_2Cl_2 was removed using a rotary evaporator. The solid residue was redissolved in THF and the crude product was crystallized from a THF/hexane mixture. Recrystallization from this solvent mixture led to the isolation of brick-red crystals of **1**·2THF. The best yield of the product was 14%. − $C_{65}H_{62}Co_3N_8O_9$ (1276.2): calcd. C 61.17, H 4.90, N 9.41; found C 60.49, H 4.88, N 9.60. − IR (KBr and Nujol): $\tilde{\nu}$ = 1591 (s), 1546 (s, br), 1521 (s, br), 1484 (s, br), 1450 (s), 1391 (s, br), 1377 (s), 1319 (m), 1308 (m, sh), 1225 (m), 1194 (w), 1180 (m, br), 1061 (s), 1025 (w), 999 (w), 951 (w), 751 (m, br), 740 (m), 721 (m), 687 (m), 626 (w), 581 (w, br), 543 cm^{-1} (w, br). − UV/Vis: λ (ε) = 537 nm ($3.26\cdot10^2$ mol^{-1}·dm^3·cm^{-1}).

Crystallographic Studies: Crystal data, together with details of the refinement, are given in Table 2. All measurements were made with a Kuma KM4CCD κ-axis diffractometer using graphite-monochromated Mo-K_α radiation. The crystal was positioned 65 mm from the KM4CCD camera; 612 frames were measured at 0.75° intervals with a counting time of 25 s. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs. The structure was solved by direct methods (program SHELXS-97[25]) and refined by the full-matrix least-squares methods on all F^2 data using the program SHELXL-97.[26] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in geometrical positions and were not refined. The crystallographic data have been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. and are available on quoting the deposition number CCDC-150406.

Magnetic and Spectral Measurements: The magnetic susceptibility was measured as a function of temperature in the range 14−300 K using a Quantum Design SQUID magnetometer (type MPMS-5). Magnetic moments were calculated for the molecule of **1**·2THF after considering the appropriate diamagnetic corrections. − ^{1}H NMR spectra were recorded with a Bruker AMX 300 MHz instrument, while X-band EPR spectra were measured with a Bruker ESP 300E spectrometer, both for a solid sample and for a solution of **1** in toluene, at 77 K and at ambient temperatures. − UV/Vis spectra in appropriate solvents and IR spectra (Nujol mulls; KBr discs) were recorded with HP 8453 diode-array and Bruker IFS113V FT-IR spectrophotometers, respectively.

Catalytic Tests: The catalytic activity of **1** was tested in oxidations of various organic substrates using *tert*-butyl hydroperoxide (TBHP) and dioxygen as oxidants in chlorobenzene and acetonitrile solution at 348 K. The progress of reactions was monitored by iodometric titration of TBHP and by volumetric measurement of dioxygen consumed. The products were separated and determined

Table 2. Crystal data and structure refinement

Empirical formula	$C_{65}H_{62}N_8O_9Co_3$
Molecular mass	1276.02
T [K]	100(2)
λ [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	13.618(3)
b [Å]	14.241(3)
c [Å]	16.069(3)
α [°]	86.69(3)
β [°]	72.47(3)
γ [°]	73.40(3)
V [Å^3]	2846.4(10)
Z	2
D_c [Mg·m^{-3}]	1.489
μ [mm^{-1}]	0.932
F(000)	1322
Crystal size [mm]	0.20 × 0.15 × 0.15
Crystal color and habit	brick-red prisms
Diffractometer	Kuma KM4CCD
θ range for data collection [°]	3.23−28.84
Index ranges	$-18 \le h \le 17$ $-15 \le k \le 18$ $-21 \le l \le 21$
Reflections collected	20661
Independent reflections (R_{int})	12971 (0.0322)
Observed reflections ($I \ge 2\sigma_I$)	7791
Data/parameters	12971/766
Weighting scheme: a, b, c[a]	0.0297, 0, 3
Goodness-of-fit (F^2)	0.851
Final R_1/wR_2 indices (obs. refl.)[a]	0.0380/0.0699
Final R_1/wR_2 indices (indep. refl.)	0.0802/0.0761
Largest diff. peak/hole [e·Å^{-3}]	0.881/−0.397

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/c$.

by GC-MS using a HP 5890 series II chromatograph coupled to a HP 5971 A mass spectrometer. The decomposition of 0.28 M TBHP in the presence of $5.2 \cdot 10^{-4}$ M **1** in chlorobenzene at 348 K was monitored by iodometric titration. The half-life for the conversion was found to be 80 min. The products of TBHP decomposition (75% conversion after 180 min) were identified and determined by GC-MS as *tert*-butyl alcohol and a trace amount of bis(*tert*-butyl) peroxide. The results of the oxidation tests are summarized in Table 1.

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