# Brief Communications

## Monoacetylferrocene crystallization in supercritical carbon dioxide

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An organometallic compound, monoacetylferrocene, was for the first time obtained as single crystals by crystallization from supercritical carbon dioxide. This offers the possibility of utilizing supercritical media for efficient crystallization and purification of organometallic compounds without using organic solvents.

**Key words:** supercritical carbon dioxide, crystallization, monoacetylferrocene, X-ray structural analysis.

Morphology changes of organic substances upon crystallization from organic solvents are well known and are practically used for purification. However, only a few examples of morphology changes or crystallization of organic or, moreover, organometallic compounds from supercritical solvents are available. For instance, changes in the degree of crystallinity of certain polymers (in particular, poly(ethylene terephthalate)[1,2] and polycaprolactone[2]) on storage in supercritical carbon dioxide were reported. It is also possible to control the morphology of $CaCO_3$ co-precipitated from a $Ca(OH)_2$—$H_2O$—$CO_2$ mixture.[3] Boron nitride crystallization from supercritical ammonia and water at high pressures (up to 5.2 GPa) and temperatures (up to 1600 K) was studied.[4] A new polymorph of fluticasone propionate steroid was obtained[5] by crystallization from supercritical ethanol or acetone.

In this work we for the first time obtained single crystals of an organometallic compound, monoacetylferrocene (MAF), by crystallization from supercritical $CO_2$. We also studied the MAF purification by crystallization from this unusual medium. This opens prospects for utilizing supercritical media for efficient purification of organometallic compounds without using organic solvents.

### Experimental

Experiments in supercritical $CO_2$ (critical pressure $P_{cr}$ = 7.38 MPa, critical temperature $T_{cr}$ = 31.1 °C, density at the critical point $\rho_{cr}$ = 470 kg m$^{-3}$) were carried out using a setup described earlier.[6,7] A stainless steel cell of volume 10 cm$^3$ was charged with 500 mg of X-ray amorphous MAF powder (Fig. 1, *a*), blown with dry $CO_2$ to remove air, heated to 60 °C, and a $CO_2$ pressure of 20 MPa was produced with a handy high pressure generator (volume 90 mL, High Pressure Equipment, USA). The cell was kept under these conditions for 2 h. The pressure generator and the cell were equipped with mechanical manometers for pressure control and with a system of valves for

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$CO_2$ feeding and decompression arranged in the upper part of the cell. The temperature was maintained with an accuracy of at least ±0.2 °C. The pressure in the cell was maintained with an accuracy of ±0.1 MPa. Decompression was done using a fine-adjustment needle valve over a period of 10 min. After crystallization, MAF was obtained as light-yellow single crystals (Fig. 1, *b*, *c*; upper part of the cell) and as finely disperse powder (Fig. 1, *d*; bottom part of the cell), which were analyzed using an Axiolab Pol (Zeiss) polarization microscope with crossed and non-crossed polaroids. The presence of the finely disperse phase can indicate both a limited MAF solubility in supercritical $CO_2$ under the experimental conditions and the presence of impurities (in the starting powder) that are removed in the course of crystallization.

Light-yellow single crystals were studied by X-ray analysis. The crystals of MAF ($C_{12}H_{12}FeO$, M = 228.07) were monoclinic, space group $P2_1/c$, at $T$ = 120 K: $a$ = 20.448(3) Å, $b$ = 5.6978(7) Å, $c$ = 18.761(2) Å, β = 116.945(2)°, $V$ = 1948.5(4) Å$^3$, $Z$ = 8, $d_{calc}$ = 1.555 g cm$^{-3}$, $F(000)$ = 944, and μ = 1.506 mm$^{-1}$. The unit cell parameters and the intensities of 17823 reflections ($R_{int}$ = 0.0956) were measured on a Bruker SMART 1000 CCD automated diffractometer equipped with an Oxford CryoSystem low-temperature accessory ($T$ = 120 K, Mo-Kα radiation, graphite monochromator, φ- and ω-scanning techniques, $2\theta_{max}$ = 54°). The structure was solved by the direct method and refined by the full-matrix least squares method anisotropically for the non-hydrogen atoms. The hydrogen atoms were located in difference Fourier syntheses and refined using fixed positional and thermal parameters. Hydrogen atoms of a Me group in one of the two independent molecules are disordered over two positions with a population ratio of 0.7 : 0.3. The final refinement parameters are as follows: $R_1$ = 0.051 for 2535 independent reflections with $I > 2\sigma(I)$ and $wR_2$ = 0.118 for all 4245 independent reflections. Calculations were carried out using the SHELXTL PLUS (Version 5.10) program package.[8]

Tables of atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic thermal parameters for MAF were deposited at the Cambridge Structural Database.

## Results and Discussion

Ferrocene derivatives are the largest and best known class of organometallic complexes.[9] Monoacetylferrocene was chosen as a model compound because the structure of the MAF crystals obtained by traditional methods was studied earlier.[10—13]

The shape of the MAF crystals (at different magnification) can be seen in Fig. 1, *b* and *c*. The crystals are needle-shaped and anisotropic (non-transparent in crossed polaroids).

The structure of MAF was studied by X-ray analysis. The molecular structure of the compound is shown in Fig. 2.

Geometric parameters of MAF obtained in this work at 120 K were identical to those of MAF that was recrystallized from a benzene—hexane mixture and studied ear-

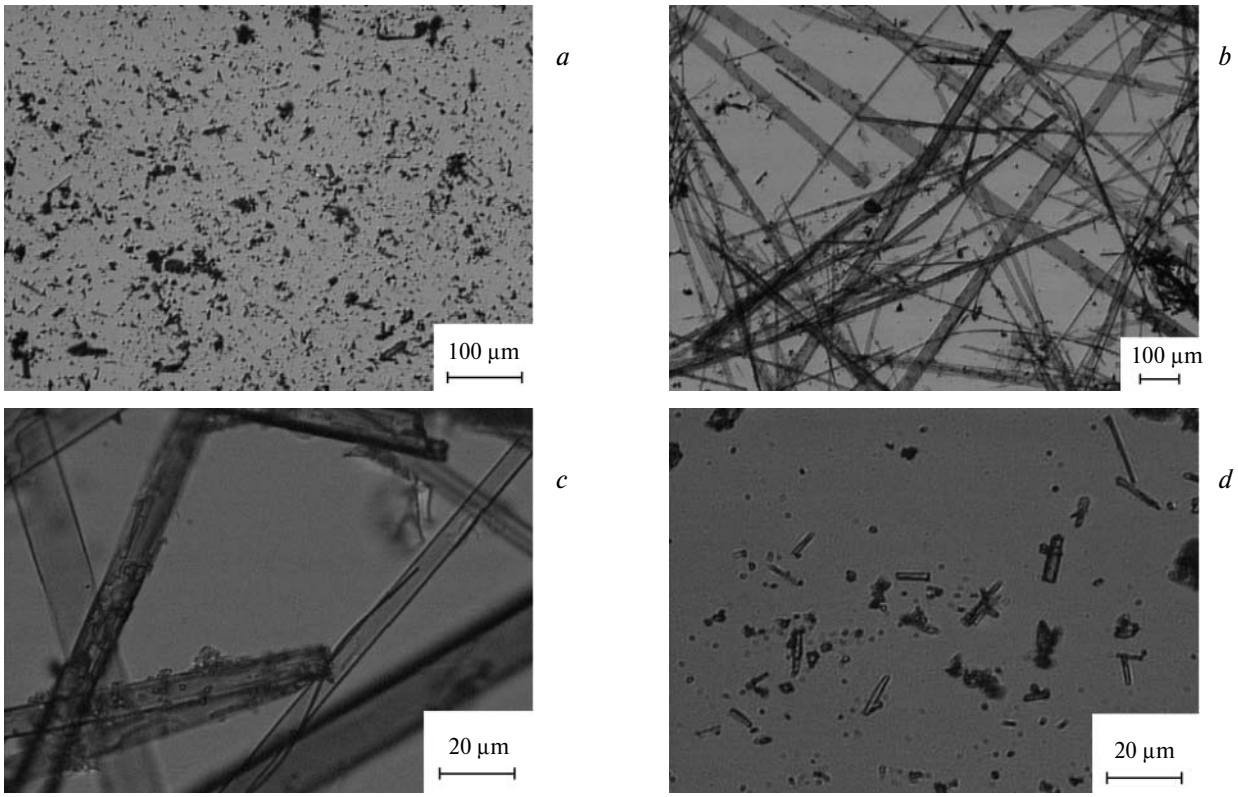


**Fig. 1.** Visual appearance of starting X-ray amorphous MAF powder (*a*), light-yellow MAF single crystals at different magnifications (*b*, *c*), and finely disperse MAF phase (*d*).

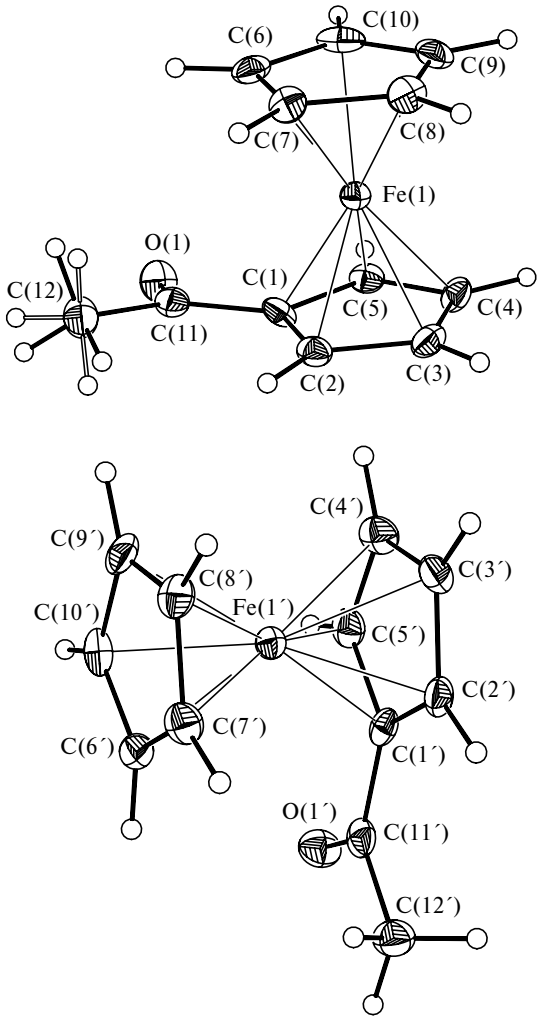


**Fig. 2.** MAF molecular structure represented by thermal probability ellipsoids ($p = 50\%$). Shown are two independent molecules. For one molecule, solid lines denote the alternative positions of hydrogen atoms of one Me group.

lier by X-ray analysis at room temperature[10—12] and at 100 K.[13] The only distinction between the structures studied is a residual disorder of hydrogen atoms of a Me group (0.7 : 0.3) in one of two independent MAF molecules at 120 K (see Fig. 2), whereas at room temperature the hydrogen atoms of all Me groups are equiprobably disordered while at 100 K this type of disorder is absent. Since the symmetry and parameters of the MAF crystal (including the thermal expansion coefficients) remain unchanged in the range 100—293 K, we can conclude that the compound undergoes no phase transitions in this temperature interval and the disorder mentioned above is dynamic in character.

Thus, we first demonstrated the possibility of crystallization of an organometallic compound, monoacetylferrocene, from supercritical carbon dioxide. The technique is environmentally safe, efficient, and can be employed for crystallization or purification of various organoelement and organometallic compounds. One can also expect that this approach will be promising for the preparation of novel crystalline forms and polymorphs of practically valuable compounds whose crystalline forms were previously obtained by traditional methods.

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