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First high thermally stable organo–inorganic 3D polymer scandium derivative as a heterogeneous Lewis acid catalyst

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$Sc_2(OOCC_2H_4COO)_{2.5}(OH)$, a new hybrid organic–inorganic polymer, has been hydrothermally obtained; the crystal structure of this material has been established by single crystal X-ray diffraction; having high thermal stability it can be used as an effective Lewis acid catalyst and can be easily recycled and reused without any appreciable loss in activity.

It is well known that three-dimensional metal–organic polymer materials possess frequently a number of interesting features such as zeolite-like catalytic, magnetic and non-linear optical properties.[1] The research in this area has resulted in many new unique 3d- and 4f-metal containing micro- and nanoporous phases[2] in which properties of all the individual components are combined in resulting hybrid materials. The di- and polycarboxylates are usually used as multifuncional ligands, which act as building blocks to construct porous coordination polymers. Among them, succinic acid has a great ability to construct coordination architectures with metal ions of diverse sizes and shapes, adopting different coordination fashions.

Though the chemistry of rare earth elements and 3d metals containing organic–inorganic polymers is developing rapidly, to the best of our knowledge, there do not exist examples of hybrid organic–inorganic scandium polymers despite their potential applications in solid-state technology and catalysis. To try to incorporate scandium, one of the least studied 3d elements, into open frameworks seemed to us very challenging.

Interest in scandium has increased recently due to the successful use of its compounds in organic chemistry[3,4] as powerful catalysts. Up to the moment, scandium triflate, $[Sc(O_3SCF_3)_3]$, is the most used scandium catalyst.[5,6] Its scope has included the use as a Lewis acid catalyst in homogeneous catalysis for electrophilic substitution, Friedel–Crafts acylations, Michael additions, Diels–Alder and Mukaiyama reactions. While Friedel–Crafts acylation reactions are fundamental in industrial chemistry,[7] reactions of acetal formation are also of great interest as one of the most useful protecting methods for carbonyl compounds,[8] usually in the presence of acid catalysts.[9] Here, we present the synthesis and crystal structure of the first organo–inorganic 3D polymer scandium derivative and a preliminary study of its catalytic activity in Friedel–Crafts acylation reaction and in the reaction of benzaldehyde acetylization.

The compound was prepared by the reaction of Sc^{3+} ions with succinic acid under hydrothermal conditions. Typically, for the preparation of the scandium succinate, 0.319 g (1 mmol) of scandium nitrate pentahydrate and 0.177 g, (1.5 mmol) of succinic acid were mixed in 5 ml of water. After adjusting the pH value to 6 by addition of triethylamine (*ca.* 0.5 ml), the reaction mixture was stirred to homogeneity in a 25 ml PTFE bottle and sealed in a stainless steel autoclave (PARR, USA). The reaction was carried out at 170 °C for ten days under autogenous pressure and afterwards cooled down slowly at a rate of 10 °C h^{-1}.

The resulting product was obtained as a single phase of colourless prismatic crystals. It was filtered off, washed thoroughly with distilled water, ethanol and ethyl ether and dried at room temperature.

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A suitable single crystal of this compound was selected and mounted in a diffractometer equipped with a CCD detector. Upon determining the crystal structure,[10] the composition was found to be $Sc_2(O_2CC_2H_4CO_2)_{2.5}(OH)$ (**I**), a scandium polymeric frame. Each scandium atom is octahedrally coordinated to six oxygen atoms, which includes five different carboxylate groups of the ligand and a μ-hydroxy group between Sc(1) and Sc(2) (Fig. 1), with bond lengths between 2.048 and 2.137 Å (usual distances for six-coordinated scandium complexes[3]) and O–Sc–O angles ranging from 85.0 to 177.3°. The two crystallographically independent Sc polyhedra share the OH group corner, giving rise to Sc_2O_{11} bioctahedral units, which are joined among them through the succinic anions. Every oxygen atom of the succinic acid coordinates to one different scandium atom in such a way that all three succinate anions act as bridging tetratopic connectors (see Fig. 2). The structure can be thought as formed by slabs of Sc_2O_{11} dimers joined through the carboxylic terminal anions. These pseudo-layers are parallel to the *ab* plane. Along the *c* direction the Sc_2O_{11} dimeric units are triply and alternatively connected with the corresponding dimers of the up and down adjacent layers, giving rise to a (6,3) honeycomb arrangement.

In the IR spectrum of **I**, the antisymmetric $\nu_{asym}(C{=}O)$ vibrations appear in the range 1610–1540 cm^{-1}, the band corresponding to the symmetric $\nu_{sym}(C{=}O)$ vibrations being found in the 1440–1390 cm^{-1} range. In addition, the bands $\nu_{sym}(O–C–O)$ and $\delta(O–C–O)$ were found at 1230 and 804 cm^{-1}, respectively. The value of $\Delta\nu = 160\ cm^{-1}$, the difference between the two wavenumbers, $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$, confirms the bridging mode of the carboxylate groups in the compound. The presence of the bridging hydroxyl group in the compound is confirmed by the appearance of a narrow band at ~3555 cm^{-1} in the expected range for ν(Sc–OH) stretching frequencies.[11]

Thermogravimetric and differential thermal analyses[12] (TGA–DTA) of **I**, have shown that the compound is stable up to 500 °C, which is a quite unusually high thermal stability for carboxylate frameworks.

In the course of the preliminary studies of catalytic properties of the new material **I**, it was found that a small amount of **I** (< 5 mol%) catalyzed the Friedel–Crafts acylation reaction of anisol

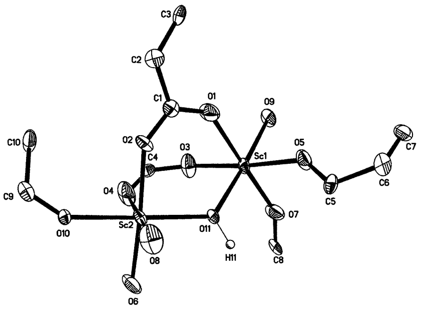

Fig. 1 ORTEP plot of the asymmetric unit.

with acetic anhydride giving the acetylated product in 30% yield after 24 h of reaction. The main reaction product was *p*-methoxyacetophenone, although a small amount of *o*-methoxyacetophenone (< 2%) was produced. It was also shown that **I** is an active and selective catalyst for acetalization of aldehydes. The reaction of benzaldehyde with trimethyl orthoformate proceeds with high conversion and the corresponding dimethyl acetal is obtained in up to 70% yield, (TON = 175 mmol substrate/mmol cat.), in relatively short reaction time (4 h) and under mild conditions (60–70 °C), using the Sc compound (8 mol%) as catalyst. Thus, the protection of aldehydes by formation of the corresponding dimethyl acetals has been carried out successfully using **I** as acid catalyst. It is noticed that while most Lewis acids are decomposed or deactivated in the presence of water, the new heterogeneous Lewis catalyst **I** is stable both in water and organic solvents and could be easily recovered by filtration and reused at least in four cycles without loss of yield or selectivity. Geometrical constraints do not allow the reactants to diffuse inside the pores of the catalyst and only the external surface area of this material becomes available to the reactants.

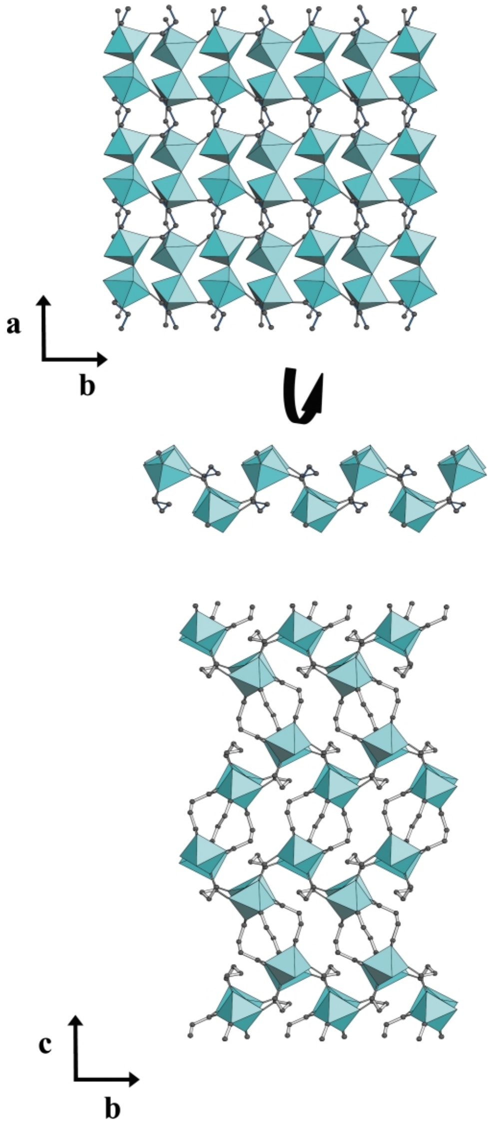

Fig. 2 Crystal structure of $Sc(OOCC_2H_4COO)_{2.5}(OH)$.

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10 *Crystal data* for **I**: empirical formula: $Sc_2(OOCC_2H_4COO)_{2.5}(OH)$; M_w = 397.11, crystal system: monoclinic; space group: $P2_1/c$; unit cell dimensions: a = 9.196(2), b = 7.857(2), c = 19.894(5) Å; β = 95.948(5)°; V = 1429.6(6) Å^3; Z = 4; T = 296(2) K; D_c = 1.845 Mg m^{-3}, μ(Mo-Kα) = 1.007 mm^{-1}; crystal size in mm: 0.4 × 0.1 × 0.1; no. of independent reflections = 3547, only 30% of the unique data has been observed, because the reflections for this compound were weak. R_1 = 0.067 for $I > 2\sigma(I)$ reflections. CCDC 196098. See http://www.rsc.org/suppdata/cc/b2/b210034g/ for crystallographic data in CIF or other electronic format.

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12 *TGA and DTA* for **I** were carried out under N_2 gas flow (50 ml min^{-1}) with a heating rate of 5 °C min^{-1}, from 25 to 900 °C. A unique and abrupt weight loss around 520 °C, corresponding to the combustion of the organic moiety (theoretical weight loss 63.45%, observed 63.50%) accompanied by an endothermic effect, leads to a complete decomposition of the framework, yielding Sc_2O_3.