Synthesis and structure of the trinuclear complex $Mn_3(\mu,\eta^2\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_2[OC(Bu^t)OHNEt_3]_2$ and the binuclear complex $Mn_2(\mu\text{-}OOCBu^t)_4[OC(Bu^t)OHNEt_3]_2$ with the 'Chinese lantern' structure

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The treatment of the product of a thermal reaction of manganese(II) acetate tetrahydrate and trimethylacetic acid with triethylamine under reflux results in the unusual complex $Mn_3(\mu,\eta^2\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_2[OC(Bu^t)OHNEt_3]_2$, which, according to X-ray diffraction analysis, incorporates a linear Mn_3 metal skeleton and four chelate-bridging trimethylacetate anions; a similar reaction at room temperature yields the $Mn_2(\mu\text{-}OOCBu^t)_4[OC(Bu^t)OHNEt_3]_2$ complex, which has a 'Chinese lantern' structure with the Mn···Mn distance equal to 3.1087(8) Å.

The chemistry of transition metal carboxylates attracts special attention owing to the unusual geometry of the resulting complexes, which is responsible for their unique physicochemical properties.[1–2]

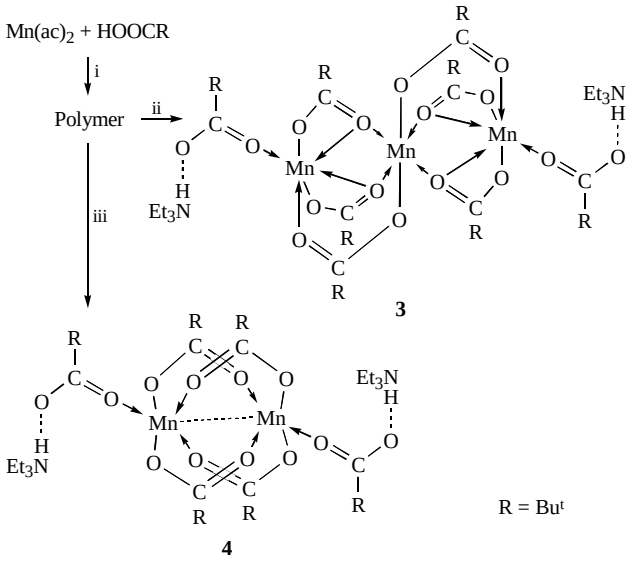
We found previously that the reaction of triethylamine with the polymeric complex obtained by fusion of cobalt(II) acetate with trimethylacetic acid results in $Co_3(\mu\text{-}OOCBu^t)_6(NEt_3)_2$ complex **1**, the structure of which changes dramatically with temperature: at 112 K, compound **1** is reversibly converted into $Co_3(\mu,\eta^2\text{-}OOCBu^t)_2(\mu\text{-}OOCBu^t)_4(NEt_3)_2$ complex **2** containing two chelate-bound bridging carboxylate ligands.[3–4]

It had to be anticipated that upon transition from cobalt(II) (d^7) to manganese(II) (d^5), a similar reaction should result in a Mn_3 complex, in which the four bridging ligands would be chelate-bound.

Indeed, it was found that the reaction of the compound obtained by fusion of manganese(II) acetate tetrahydrate and trimethylacetic acid† with an excess of triethylamine in heptane under reflux resulted in the colourless complex $Mn_3(\mu,\eta^2\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_4[OC(Bu^t)OHNEt_3]_2$ **3** (Scheme 1).‡

According to the X-ray diffraction analysis of compound **3** (Figure 1),§ three Mn^{II} atoms are arranged along a common line at the nonbonding distances Mn···Mn of 3.408(1) Å. The central 17-electron manganese atom appears in an octahedral environment of six oxygen atoms, two of which are parts of two μ-bridging trimethylacetate moieties, [Mn(2)–O(2)(2A) 2.126(2) Å]. The remaining four oxygen atoms belong to four bridging trimethylacetate fragments, which are η^2-bound with two peripheral 17-electron manganese atoms; the latter have a distorted octahedral environment complemented by the oxygen atom of the terminal trimethylacetate anion, which forms a hydrogen bond with the Et_3NH cation.

Trinuclear carboxylate complexes of manganese(II) with linear metal skeletons are well known: all of them contain two monodentate or bidentate peripheral O- or N-donor ligands and have structures similar to those observed in compounds **1** and **2**,



Scheme 1 *Reagents and conditions*: i, fusion at 150 °C; ii, Et_3N, hexane, 50 °C, 30 min; iii, Et_3N, hexane, 22 °C.

depending on the nature of the donor and substituent R.[5,6] The type of bridging interaction with two chelate-bound carboxylate fragments discovered in complex **3** was encountered for the

† Fusion of manganese(II) acetate tetrahydrate (1 g) with trimethylacetic acid (7 g) at 165 °C for 1.5 h results in a pink-brown gel-like mass, which hardens on cooling. The resulting dry powder with unknown structure was washed with cold hexane and dried in a stream of argon. The yield was 1.3 g. IR (KBr, ν/cm^{-1}): 3436 (m.w), 2962 (s), 2930 (w), 2873 (w), 2576 (w.w), 1678 (m), 1556 (s), 1483 (s), 1460 (w), 1421 (s), 1362 (s), 1227 (s), 1207 (m), 1031 (w), 937 (w), 896 (w), 873 (w), 789 (m), 601 (m), 538 (m), 417 (m).

‡ The white-pink powder of the manganese compound (1.2 g) was dissolved in Et_3N (3 ml); hexane (5 ml) was added, and the resulting mixture was refluxed for 30 min. The resulting pale pink solution was slowly cooled to room temperature in an oil bath. The large colourless prisms precipitated were separated from the solution by decantation, washed with cold pentane and dried in a stream of argon. The yield of compound **3** was 0.9 g. IR (KBr, ν/cm^{-1}): 3441 (m.w), 2958 (s), 2926 (m), 2869 (m), 1558 (s), 1483 (s), 1457 (m), 1416 (s), 1373 (m), 1358 (m), 1315 (w), 1282 (w), 1227 (s), 1187 (w), 1152 (w), 1031 (m), 893 (s), 835 (m), 799 (m), 790 (s), 600 (s), 552 (w), 535 (m), 417 (m), 385 (m).

§ X-Ray diffraction experiments were carried out at the Centre for Structural Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) by a standard procedure[8] using a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo, graphite monochromator, ω-scanning, scanning step of 0.3°, frame measurement time of 10 s, $2\theta_{max}$ = 54°). For compound **3**: $C_{52}H_{104}Mn_3N_2O_{16}$, M = 1178.9, space group $P2_1/c$, a = 13.896(3), b = 19.305(4), c = 12.577(2) Å, β = 104.231(4)°, V = 3270.3(11) Å^3 (120 K), Z = 2; 31025 measured reflections including 7126 independent reflections with $F^2 > 2\sigma(I)$, d_{calc} = 1.196 g cm^{-3}, μ = 6.29 cm^{-1}, R_1 = 0.0614, wR_2 = 0.1459. For compound **4**: $C_{42}H_{86}Mn_2N_2O_{12}$, M = 921.01, space group $C2$, a = 20.7932(18), b = 11.7616(10), c = 13.1808(12) Å, β = = 125.877(2)°, V = 2611.9(4) Å^3 (200 K), Z = 2, 6766 measured reflections including 5217 independent reflections with $F^2 > 2\sigma(I)$, d_{calc} = = 1.171 g cm^{-3}, μ = 5.36 cm^{-1}, R_1 = 0.0686, wR_2 = 0.1196. The crystals of **4** are destroyed at 120 K. All atoms of four thrimetylacetate anions and the Et groups of Et_3NH fragments in the molecule of **4** are disordered over two positions with an occupancy of 0.5. The positions of all hydrogen atoms in compounds **3** and **4** were calculated geometrically.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 238620 and 238621. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

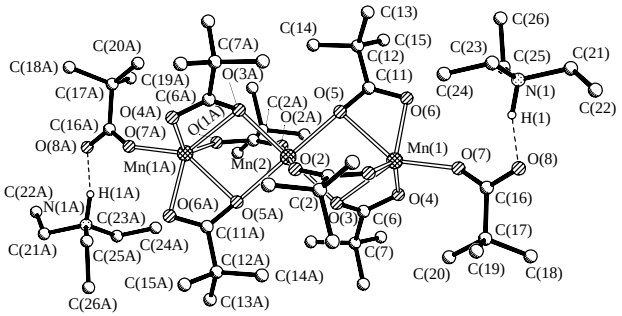


Figure 1 Structure of complex **3**. Selected bond lengths (Å) and angles (°): Mn(2)–O(3)(3A) 2.186(2), Mn(2)–O(5)(5A) 2.193(2), Mn(1)–O(1) 2.065(2), Mn(1)–O(4) 2.160(2), Mn(1)–O(6) 2.189(2), Mn(1)–O(3) 2.483(3), Mn(1)–O(5) 2.378(2), Mn(1)–O(7) 2.069(2), angle Mn(1)–Mn(2)–O(7) 168.8, N(1)···O(8) 2.650, H(1)···O(8) 1.62.

first time, not only for manganese(II) complexes but also for complexes of other 3*d* metals.

A similar reaction carried out at room temperature¶ gave colourless binuclear complex $Mn_2(\mu\text{-}OOCBu^t)_4[OC(Bu^t)OHNEt_3]_2$ **4**, as the main product (Scheme 1). According to X-ray diffraction analysis, the molecule of **4** (Figure 2)§ has a 'Chinese lantern' geometry; two Mn^{II} atoms located at a distance of 3.1087(8) Å are bound by four trimethylacetate bridges [Mn–O 2.051(15)–2.108(15) Å]. The distorted tetragonal-pyramidal environment of each manganese atom is complemented by an oxygen atom belonging to the $OC(Bu^t)OHNEt_3$ fragment [Mn–O(5) 2.040(1) Å; the Mn(1)–Mn(1A)–O(5A) angle equals 178.2°], in which the hydrogen atom of the Et_3NH cation forms a short bond with the oxygen atom of the trimethylacetate ligand, which is axial with respect to the Mn–Mn line [N(1)···O(6) 2.672 Å, O(6)–H 1.57 Å]. Note that two carboxylate Mn^{II} complexes with 'Chinese lantern' structures have been obtained previously; however, they contained coordinated quinoline molecules in axial positions, unlike complex **4** obtained in this work.[7]

¶ The white-pink powder of the manganese compound (1.0 g) was dissolved in Et_3N (3 ml), and hexane (10 ml) was added at room temperature. The resulting pale pink homogeneous solution was kept at 5 °C in a refrigerator. The large colourless prisms precipitated were separated from the solution by decantation, washed with cold pentane and dried in a stream of argon. The yield of compound **4** was 0.5 g. IR (KBr, ν/cm^{-1}): 3443 (br. m), 2977 (s), 2958 (s), 2906 (m), 2871 (m), 2738 (w), 2678 (m), 2491 (w), 1698 (m), 1629 (s), 1551 (vs), 1483 (s), 1458 (m), 1417 (vs), 1370 (s), 1310 (w), 1227 (s), 1150 (w), 1080 (w), 1034 (w), 937 (w), 890 (m), 833 (m), 789 (m), 748 (w), 600 (m), 554 (m), 535 (m), 413 (m).

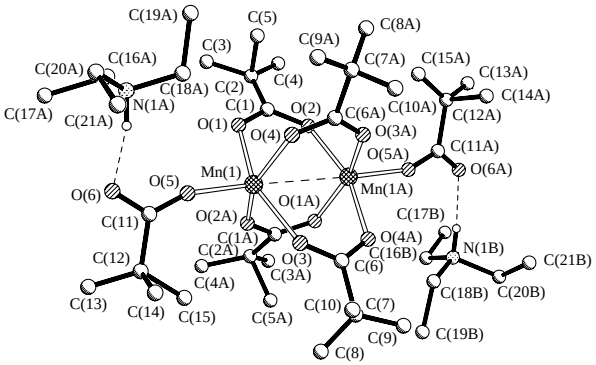


Figure 2 Structure of complex **4**.

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