Synthesis and Reactivity of *N*,*N*-Dialkylcarbamato Complexes of Manganese(II). Crystal and Molecular Structure of $[Mn_6(O_2CNEt_2)_{12}]$, a Hexamer with Four Five-co-ordinated Manganese(II) Atoms†

Antonio Belforte and Fausto Calderazzo *
Dipartimento di Chimica e Chimica Industriale, Sezione Chimica Inorganica, Universitá di Pisa, via Risorgimento 35, 56100 Pisa, Italy
Pier Francesco Zanazzi
Dipartimento di Scienze della Terra, Sezione Cristallografia, Universitá di Perugia, Piazza Universitá, 06100 Perugia, Italy

The compounds $[\{Mn(O_2CNR_2)_2\}_n]$ (R = Me, Et, or Pr^i) have been prepared by treating $[Mn(cp)_2]$ (cp = η^5-C_5H_5) with CO_2–NHR_2 in organic solvents. These reactions may possibly involve the addition compound $[Mn(cp)_2]\cdot NHR_2$. In the case of R = Et, the adduct has been isolated and characterized, and the space group, crystal data, and metal connectivity established. The structure of the *N*,*N*-diethylcarbamato complex has been solved by *X*-ray diffraction. Crystal data: monoclinic, space group *C*2/*c*, $a = 18.546(3)$, $b = 19.287(3)$, $c = 24.877(3)$ Å, $\beta = 95.38(2)°$, $R = 0.078$. It consists of hexameric units $[Mn_6(O_2CNEt_2)_{12}]$, containing four five-co-ordinated Mn atoms, joined by bridging carbamato ligands. It was found to be unreactive towards nucleophiles, while by reaction with $[\{Ti(cp)_2Cl\}_2]$ the new complex $[Ti(cp)_2(O_2CNEt_2)]$ has been obtained. Organic electrophiles react regioselectively at the oxygen or at the nitrogen atom of the carbamato ligand of the manganese complexes, and in the former case the CO_2 fragment is retained in the reaction products.

Some years ago our research group became interested in the chemistry of transition-metal carbamato complexes, of general formula $[\{M(O_2CNR_2)_n\}_m]$.[1] We found a synthetic procedure based on the exchange reaction between a metal halide and the dialkylcarbamate obtained by the *in situ* interaction of a secondary amine with carbon dioxide,[1f] see reactions (1) and (2).

$$CO_2 + 2\,NHR_2 \rightleftharpoons [NH_2R_2]^+\,[R_2NCO_2]^- \qquad (1)$$

$$MX_n + n[NH_2R_2]^+\,[R_2NCO_2]^- \longrightarrow [M(O_2CNR_2)_n] + nNH_2R_2X \qquad (2)$$

Recently[2] we showed that these complexes can be used as intermediates to accomplish electrophilic reactions on the carbon dioxide molecule. The present interest[3] in CO_2 as a building block stimulated us to extend our investigation, and to look for the effect of different metals upon the reactivity of the carbamato group. Moreover, carbamates are often found in biological systems, and those bound to bivalent cations have been suggested to be involved in important processes related to carbon dioxide biochemistry, such as the biotin-mediated carboxylation,[4] the bacterial synthesis of methane from CO_2,[5] and the fixation of CO_2 in the photosynthetic Calvin cycle.[6] The d^5 Mn^{2+} ion is present in some biotin-containing enzymes,[7] and can replace alkaline-earth-metal ions in ribulose bis(phosphate) carboxylase.[6] However, its role and the detailed mechanism of incorporation of CO_2 has not yet been clarified. The co-ordination environment of manganese in the protein is not known, and only a brief mention of manganese carbamato complexes can be found in the literature.[8]

In this paper we report a synthetic and structural study of *N*,*N*-dialkylcarbamates of manganese(II), and describe some of their reactivity.

Results and Discussion

Synthesis and Structure.—The simplest route to *N*,*N*-dialkylcarbamato complexes of manganese(II) appeared to be the well established reaction (2), and we tested its application in the case of the $MnCl_2$–NHR_2 system, R being Me, Et, or Pr^i. While in the case of R = Et this represented a good synthetic method, it failed in the other cases due to the low solubility of some of the reaction products; the failure to obtain a pure product was attributed to the use of $MnCl_2$. Wilkinson *et al.*[9] suggested that $[Mn(cp)_2]$, cp = η^5-C_5H_5, may show ionic behaviour in solution; we have found that a suspension of $[Mn(cp)_2]$ in toluene reacts easily with CO_2–NHR_2, see reaction (3), and the manganese complex can be isolated without difficulty from the organic by-products.

$$[Mn(cp)_2] + 2[NH_2R_2]^+\,[R_2NCO_2]^- \longrightarrow [Mn(O_2CNR_2)_2] + 2Hcp + 2NHR_2 \qquad (3)$$

Although we have no definite evidence, we believe that the manganese species actually reacting in solution is a $[Mn(cp)_2(NHR_2)_n]$ adduct. The addition of amines to a suspension of $[Mn(cp)_2]$ in toluene results in the ready solubilization of the solid and, in the case of $NHEt_2$, we isolated a colourless, sublimable solid, of composition $[Mn(cp)_2]\cdot NHEt_2$. The existence of addition compounds between $[Mn(cp)_2]$ and Lewis bases like amines or ethers was reported nearly 30 years ago,[9] but structural characterization has been achieved only recently for $[Mn(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(tmen)]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[10] and for $[Mn(\eta^5\text{-}C_5H_5)(PR_3)_2]$.[11] It was therefore decided to carry out an *X*-ray diffraction study on the crystals of $[Mn(cp)_2]\cdot NHEt_2$. We were unsuccessful in refining the molecular structure to a satisfactory *R* value, therefore the geometric

---

† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: 1 mmHg = 133 Pa.

Table 1. Selected bond distances (Å) and angles (°) for $[Mn_6(O_2CNEt_2)_{12}]$

Mn(1)–O(1)	2.074(15)	Mn(2)–O(5′)	2.187(12)
Mn(1)–O(3)	2.104(14)	Mn(2)–O(7′)	2.145(12)
Mn(1)–O(6)	2.216(12)	Mn(1) ··· Mn(2)	3.269(5)
Mn(1)–O(5′)	2.165(12)	Mn(3) ··· Mn(3′)	3.362(5)
Mn(1)–O(7′)	2.243(12)	Mn(3)–O(4)	2.032(14)
Mn(1)–O(9′)	2.261(12)	Mn(3)–O(6)	2.194(12)
Mn(2) ··· Mn(2′)	3.396(4)	Mn(3)–O(10)	2.061(15)
Mn(2)–O(2)	2.037(15)	Mn(3)–O(12)	2.085(16)
Mn(2)–O(8)	2.065(14)	Mn(3)–O(9′)	2.156(12)
Mn(2)–O(11)	2.111(18)	Mn(1) ··· Mn(3)	3.269(5)
O(1)–Mn(1)–O(3)	90.6(5)	O(2)–Mn(2)–O(7′)	96.5(5)
O(1)–Mn(1)–O(6)	170.0(5)	O(8)–Mn(2)–O(11)	90.8(6)
O(1)–Mn(1)–O(5′)	84.3(5)	O(8)–Mn(2)–O(5′)	87.4(5)
O(1)–Mn(1)–O(7′)	87.8(5)	O(8)–Mn(2)–O(7′)	138.8(5)
O(1)–Mn(1)–O(9′)	109.9(5)	O(11)–Mn(2)–O(5′)	162.7(6)
O(3)–Mn(1)–O(6′)	84.9(5)	O(11)–Mn(2)–O(7′)	90.3(6)
O(3)–Mn(1)–O(5′)	168.6(5)	O(5′)–Mn(2)–O(7′)	79.9(5)
O(3)–Mn(1)–O(7′)	111.7(5)	O(4)–Mn(3)–O(6)	89.6(5)
O(3)–Mn(1)–O(9′)	87.5(5)	O(4)–Mn(3)–O(10)	121.4(6)
O(6)–Mn(1)–O(5′)	101.7(4)	O(4)–Mn(3)–O(12)	104.9(6)
O(6)–Mn(1)–O(7′)	85.6(4)	O(4)–Mn(3)–O(9′)	97.7(5)
O(6)–Mn(1)–O(9′)	78.9(4)	O(6)–Mn(3)–O(10)	87.5(5)
O(5′)–Mn(1)–O(7′)	78.3(4)	O(6)–Mn(3)–O(12)	163.8(5)
O(5′)–Mn(1)–O(9′)	84.8(4)	O(6)–Mn(3)–O(9′)	81.6(4)
O(7′)–Mn(1)–O(9′)	154.2(5)	O(10)–Mn(3)–O(12)	90.7(6)
O(2)–Mn(2)–O(8)	122.8(6)	O(10)–Mn(3)–O(9′)	139.3(5)
O(2)–Mn(2)–O(11)	104.8(6)	O(12)–Mn(3)–O(9′)	89.4(5)
O(2)–Mn(2)–O(5′)	90.6(5)		

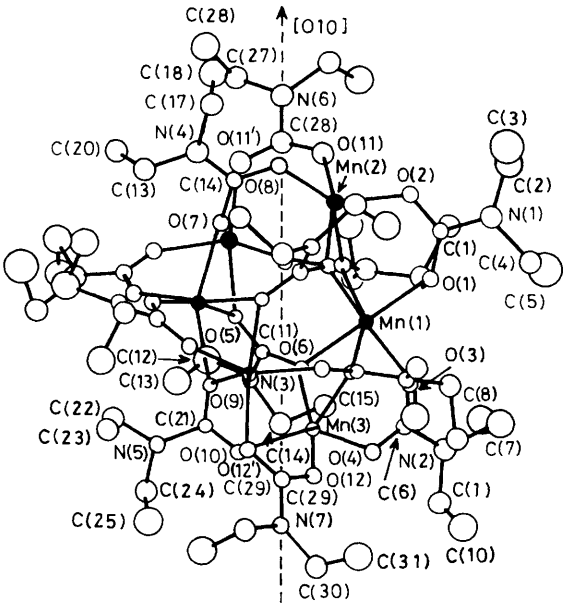


Figure 1. Structure of the hexamer $[Mn_6(O_2CNEt_2)_{12}]$ viewed along the *a* axis. Primed atoms are related to the corresponding unprimed ones by a two-fold axis of rotation

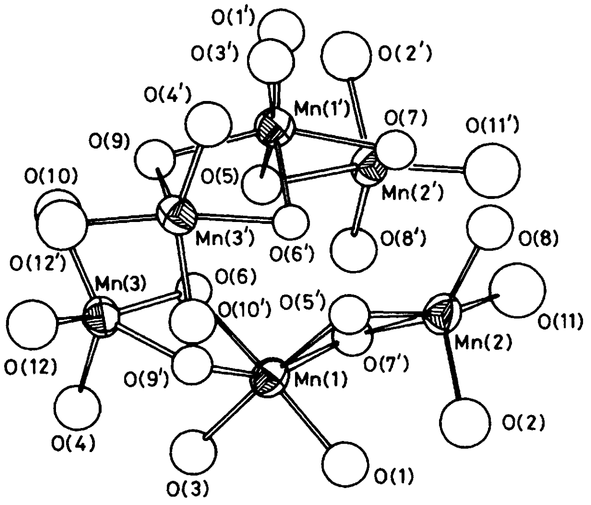


Figure 2. Co-ordination environment of the Mn atoms in $[Mn_6(O_2CNEt_2)_{12}]$

parameters will not be reported (see Experimental section). On the other hand, the connectivity within this compound was established: the manganese atom was shown to be co-ordinated to two centrosymmetric bent cyclopentadienyl groups and to the $NHEt_2$ ligand. The existence of the amine adduct and its high solubility in aromatic hydrocarbons suggest that it plays a major role in the formation of the carbamato complex.

The *N*,*N*-dialkylcarbamato ligand can participate in a large variety of binding modes, and we have found[1] that in homoleptic metal carbamato complexes it can lead to polynuclear structures of high complexity. Spectroscopic methods are ineffective in elucidating such situations, and therefore we decided to carry out an *X*-ray investigation of the ethyl derivative $[\{Mn(O_2CNEt_2)_2\}_n]$. This compound was found to be isostructural with the analogous cobalt(II) derivative,[1c] and to consist of hexameric units $[Mn_6(O_2CNEt_2)_{12}]$, one of which is shown in Figure 1, with the numbering scheme used. Selected bond distances and angles are in Table 1.

A detailed description of the structure would be redundant because of that already given for $[Co_6(O_2CNEt_2)_{12}]$,[1c] but some facts are worthy of mention. The Mn–O bond distances can be compared with those found in the cobalt analogue. There is an average lengthening of about 0.09 Å for the manganese system, in agreement with the difference in ionic radii[12] (0.08 Å) between the two cations. The bond angles are nearly identical for the two compounds in each of the three co-ordination polyhedra. A remarkable consequence of this situation is that the hexameric unit contains four five-co-ordinated manganese atoms [Mn(2), Mn(3), Mn(2′), and Mn(3′) in Figure 2], related pairwise by the two-fold rotation axis. Each of the manganese atoms is co-ordinated by five oxygen atoms in an approximate trigonal bipyramidal geometry. These oxygen atoms belong to five different carbamato groups, and, in this respect, the central atom can be regarded as co-ordinated by unidentate ligands. This situation is quite rare for manganese(II), and, to our knowledge, has been reported only for two complexes of the type MnX_2L_3.[13,14]

It is interesting to compare our structure with the recently reported[15] mixed-valence manganese carboxylate $[Mn_6O_2(Me_3CCO_2)_{10}(Me_3CCO_2H)_4]$. In the latter complex two oxygen atoms act as μ_4 ligands, in the approximate positions occupied by the two carbamato ligands engaged in co-ordination to four Mn atoms in our complex. As far as the arrangement of the twelve anionic ligands is concerned, it appears that, despite a different formulation, the carboxylato complex has a similar topological structure and a similar geometry around each manganese atom to that in our compound. A remarkable difference lies in the fact that four pivalic acids as terminal ligands complete the six-co-ordination for the four external manganese(II) atoms in the former compound, while these atoms are found to be five-co-ordinated in our carbamato complex. In view of this, and of the synthetic method used (an excess of amine was required), it is noteworthy that our complex does not contain co-ordinated $NHEt_2$, although no ligand-field stabilization energy can be present for the d^5 manganese(II), and six-co-ordination would be predicted only by a purely electrostatic model.

An explanation could possibly come from the observation that the presence of an envelope of twelve carbamato ligands seems to confer an overall thermodynamic stability upon the molecule in the crystal, the same number being observed in other structures of metal carbamato complexes that we have previously investigated, namely $[U_4O_2(O_2CNEt_2)_{12}]$,[16] $[Yb_4(O_2CNPr^i_2)_{12}]$,[1b] $[Co_6(O_2CNEt_2)_{12}]$,[1c] and $[Cu_8O_2(O_2CNPr^i_2)_{12}]$.[1g]

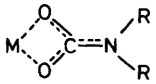
The magnetic moment of 6.00 is in agreement with the presence of magnetically dilute high-spin d^5 ions, and with the presence of non-bonding Mn • • • Mn distances in the crystal.

Of course, the molecular structure in solution may be different from that found in the solid state, and although a rather high nuclearity is maintained in hydrocarbons, as indicated by molecular-weight measurements in benzene,* we expect it to decrease on going to more polar solvents.

Reactivity.—The free carbon dioxide molecule shows a ready reactivity at the carbon atom towards nucleophilic reagents, such as Lewis bases,[3a] carbanions,[3c] and even transition metals in low oxidation state.[3b] Also some biological carboxylations can be formally viewed as involving the attack of a nucleophilic carbon on the CO_2 molecule,[4a,6a] even when it is bonded in the protein as a carbamato group.[4a,17]

It was therefore of interest to see whether the same situation holds for the CO_2 moiety in our complexes. They, however, did not show any reactivity towards nucleophilic reagents, whether organic (MgBrPh) or inorganic {Na[Mn(CO)$_5$] or Na[Fe(cp)(CO)$_2$]}. The carbamato complex $[Mn_6(O_2CNEt_2)_{12}]$ reacts with sodium metal, but electron transfer occurred at the metal, so that metallic manganese and sodium *N*,*N*-diethylcarbamate are the products.

As it could be expected on the basis of valence-bond arguments, the carbon atom of the CO_2 moiety can be supplied with electrons by the nitrogen lone pair, thus losing the electrophilic character possessed as the free molecule. This same



scheme suggests that the two oxygen atoms can show a nucleophilic behaviour, and our preliminary observations[2] confirmed that electrophilic acyl chlorides R′COCl react at the carbamato oxygens, to give metal chloride and the mixed carboxylato–carbamato anhydrides R′C(O)OC(O)NR$_2$. In the present case, we treated $[Mn_6(O_2CNEt_2)_{12}]$ with some organic and inorganic electrophiles, see Scheme. Reaction (iii) led to the synthesis of a new titanium(III) carbamato complex,[1f] for which we propose a monomeric structure on the basis of its magnetic moment (1.66, corresponding to a magnetically dilute d^1 system) and of a molecular-weight determination in solution; moreover, the corresponding carboxylato[18] and dithiocarbamato[19] titanocene derivatives are reported to be monomeric. The same [Ti(cp)$_2$(O$_2$CNEt$_2$)] was obtained directly starting from [{Ti(cp)$_2$Cl}$_2$], $NHEt_2$, and CO_2 [*cf.* reactions (1) and (2)]. Reaction (iii) is the first example of a direct exchange of a carbamato ligand between two transition metals, and constitutes a new synthetic tool in this area of chemistry. While in reactions (ii) and (iii) of the Scheme the products result from the attack of the electrophiles on the oxygen atom of the carbamato group, reaction (i) deserves further comment. The intermediacy of the unstable[2] mixed anhydride is supported, in addition to the spectral evidence reported in the Experimental section, by the isolation of the stable PhC(O)OC(O)NPr$^i_2$ from the reaction between PhCOCl and [{Mn(O$_2$CNPr$^i_2$)$_2$}$_n$]. Thus it is possible to explain the reactivity of $[Mn_6(O_2CNEt_2)_{12}]$ with the unique exchange reaction (4), where E represents the

$$[Mn(O_2CNEt_2)_2] + 2E\text{–}Cl \longrightarrow MnCl_2 + 2Et_2NCO_2\text{–}E \quad (4)$$

element (C, Si, or Ti) interacting with the nucleophilic oxygen. To extend the scope of this reaction we investigated the reactivity of $[Mn_6(O_2CNEt_2)_{12}]$ towards alkyl halides. In terms of reaction (4), this would lead to alkylurethanes directly from CO_2, a significant synthetic goal. The manganese carbamato complexes did not react with methyl iodide in n-heptane or toluene, but did so in thf. We were unable to detect any urethane in the reaction mixture, and the only products were carbon dioxide and the tetra-alkylammonium tetraiodomanganate salts, see reaction (5) (R = Et or Pr^i). This fact is in

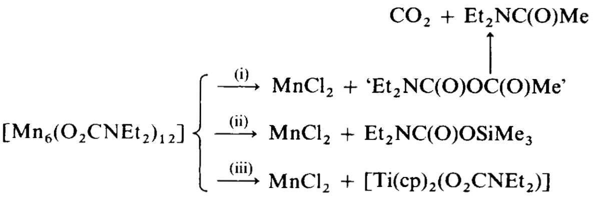
$$[Mn(O_2CNR_2)_2] + 4MeI \longrightarrow [NR_2Me_2]_2[MnI_4] + 2CO_2 \quad (5)$$

agreement with the reactivity observed for $[Co_6(O_2CNEt_2)_{12}]$.[1c] However, a different behaviour has been reported in a few cases, namely copper(I)[20] and dialkylammonium[21] carbamates reacting with MeI to give methylurethanes.

A possible explanation for the failure of our system to react at the carbamato oxygen could be the formation of a Mn–I bond, weaker[22] than the Mn–Cl bond obtained by use of the electrophilic reagents used in the Scheme. On the other hand, the weaker electrophiles Me$_2$CHBr and PhCH$_2$Cl did not react with $[Mn_6(O_2CNEt_2)_{12}]$, even with prolonged refluxing in thf. A further attempt to alkylate the carbamato group was made with the use of Me$_2$SO$_4$, but even in this case the reaction led only to the formation of the ammonium salt [equation (6)]. The

$$[Mn(O_2CNEt_2)_2] + Me_2SO_4 \longrightarrow MnSO_4 + [NMe_2Et_2]_2SO_4 \quad (6)$$

formation of the tetra-alkylammonium salt in these cases indicates that the nitrogen lone pair on the carbamato group retains at least part of its nucleophilic character. Our experimental findings, however, seem to suggest that the charge localization in the carbamato group is not a sufficient explanation of its reactivity towards electrophiles, and of the observed selectivity towards O or N. We cannot exclude a possible involvement of the metal ion in stabilizing a transition state leading to attack on oxygen. The incipient formation of a metal–chlorine bond would be an important point in this scheme. Further work is in progress to clarify the O *vs.* N selectivity for metal carbamates.



$$[Mn_6(O_2CNEt_2)_{12}] \left\{ \begin{array}{l} \xrightarrow{\text{(i)}} MnCl_2 + \text{‘}Et_2NC(O)OC(O)Me\text{’} \rightarrow CO_2 + Et_2NC(O)Me \\ \xrightarrow{\text{(ii)}} MnCl_2 + Et_2NC(O)OSiMe_3 \\ \xrightarrow{\text{(iii)}} MnCl_2 + [Ti(cp)_2(O_2CNEt_2)] \end{array} \right.$$

Scheme. (i) MeCOCl, tetrahydrofuran (thf); (ii) SiMe$_3$Cl, thf; (iii) [{Ti(cp)$_2$Cl}$_2$], toluene

---

* Cryoscopic measurements in benzene suggest some cleavage of the hexanuclear structure, the molecular weight corresponding to an average nuclearity between 4 and 5.

Experimental

All operations were carried out under an inert atmosphere of prepurified nitrogen or argon. Solvents were dried by conventional methods. The amine $NHMe_2$ was vacuum transferred in a Schlenk tube over molecular sieves and stored at −30 °C; $NHEt_2$ and $NHPr^i_2$ were distilled from sodium and stored over sodium sand. Acyl halides, chlorotrimethylsilane, and methyl iodide were distilled prior to use and kept under nitrogen. Dimethyl sulphate was used as purchased. The compounds $[Mn(cp)_2]$[9] and $[\{Ti(cp)_2Cl\}_2]$[23] were prepared by literature procedures.

Infrared spectra were recorded with a Perkin-Elmer model 283 spectrophotometer, and magnetic moments were measured in the solid state by the Faraday method. The CO_2 content of the complexes was determined from the amount of gas evolved after decomposition with 20% H_2SO_4, while manganese was determined by complexometric titration with ethylenediaminetetra-acetate.

Synthesis of $[\{Mn(O_2CNMe_2)_2\}_n]$, (**1**).—A solution of $NHMe_2$ (3.50 g, 77.6 mmol) in toluene (25 cm^3) was saturated with CO_2 at room temperature. Then $[Mn(cp)_2]$ (1.99 g, 10.7 mmol) was added, and the mixture was stirred for 16 h to give a yellow solution that was cooled to −80 °C for 5 d. The colourless precipitate thus formed was filtered off while still cold and dried *in vacuo* (2.25 g). This solid was shown by i.r. spectroscopy to contain some amine. Washing with boiling toluene and drying at 80 °C for 24 h in high vacuum gave 1.15 g of the colourless product (46% yield), only sparingly soluble in hydrocarbon solvents (Found: C, 31.8; H, 5.2; CO_2, 36.9; Mn, 22.6; N, 11.6. Calc. for $C_6H_{12}MnN_2O_4$: C, 31.1; H, 5.2; CO_2, 38.0; Mn, 23.7; N, 12.2%).

Synthesis of $[\{Mn(O_2CNEt_2)_2\}_n]$, (**2**).—A suspension of $[Mn(cp)_2]$ (3.86 g, 20.8 mmol) in toluene (150 cm^3) was treated with the stoicheiometric amount of $NHEt_2$ (3.17 g, 43.4 mmol). A yellow clear solution was obtained after a few minutes, and CO_2 was admitted to the reaction flask. After 2 h no more gas uptake was observed, and the yellow solution was evaporated to dryness to give 5.97 g (99% yield) of crude product. Its i.r. spectrum as a Nujol mull was identical with that of $[Mn_6(O_2CNEt_2)_{12}]$, see below: recrystallization from boiling n-heptane yielded compound (**3**), see below.

Interaction between $[Mn(cp)_2]$ *and* $NHEt_2$.—To a suspension of $[Mn(cp)_2]$ (1.47 g, 7.9 mmol) in toluene (50 cm^3) was added $NHEt_2$ (1.6 cm^3, 1.12 g, 15.3 mmol). The solid slowly dissolved and the clear yellow solution was cooled to −80 °C. After 3 d, 1.65 g of a colourless solid were obtained by filtration of the cold solution. Its analysis was consistent with the formulation $[Mn(cp)_2]\cdot NHEt_2$ (Found: Mn, 21.5. Calc. for $C_{14}H_{21}MnN$: Mn, 21.3%). This product was transferred to a sublimation apparatus evacuated to 0.1 mmHg. At 70 °C a colourless solid sublimed, followed at *ca.* 100 °C by the sublimation of amber $[Mn(cp)_2]$ accompanied by the release of some $NHEt_2$, which condensed in a trap cooled at −80 °C. The colourless fraction of the sublimate was collected and sealed under argon in glass vials.

X-*Ray Characterization of* $[Mn(cp)_2]\cdot NHEt_2$.—A crystal with dimensions 0.20 × 0.18 × 0.15 mm protected in a glass capillary was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å). The compound is monoclinic, with possible space groups $P2_1$ or $P2_1/m$ (from systematic extinctions). The acentric group was preferred on the basis of the distribution of intensities and the structure solution.

Crystal data. $C_{14}H_{21}MnN$, M = 258.3, a = 7.943(4), b = 11.820(5), c = 7.501(4) Å, β = 90.83(5)°, U = 704 Å^3, Z = 2, D_c = 1.21 g cm^{-3}, $F(000)$ = 274, μ = 9.28 cm^{-1}.

Two sets of equivalent reflections ($\pm hkl$ and $\pm h-kl$) were collected at room temperature in the range θ 2—20°, with the ω—2θ scan technique, scan range 1.6°, speed 0.04 ° s^{-1}. 1 250 Reflections having $I > 3\sigma(I)$ were merged to give 803 independent data for subsequent calculations. Owing to the poor quality of the diffraction data, the agreement factor between equivalent data was rather poor ($R_{eq.}$ = 0.12).

The structure was solved by Patterson and Fourier methods. The refinement was performed by the least-squares method using the SHELX 76 package of programs.[24] The structure did not refine below R = 0.11, even when thermal parameters were refined in the anisotropic mode: several thermal parameters for C atoms became negative, and a Fourier difference map revealed some residual peaks that could not be explained by reasonable atomic positions, being too near to other atoms. A new data collection with another crystal did not give better results. These facts were ascribed to severe disorder in the crystals hampering a reliable refinement.

Synthesis of $[Mn_6(O_2CNEt_2)_{12}]$, (**3**).—A toluene solution (150 cm^3) of $NHEt_2$ (35 g, 478.5 mmol) in a 1-l flask was saturated with CO_2 at room temperature, and anhydrous $MnCl_2$ (12.58 g, 100 mmol) was added. The flask was heated at 50 °C for 4 d with periodic cooling to room temperature and restoration of the pressure of CO_2. After this period, the dialkylammonium chloride was filtered off, and the pale amber solution evaporated to dryness. A glassy solid was obtained, that was totally dissolved in boiling n-heptane (120 cm^3). This solution was filtered while still hot and slowly cooled first at room temperature and then to −30 °C for 24 h. The product (18.97 g, 66% yield) was obtained as large colourless crystals after filtration of the cold solution [Found: C, 41.4; H, 6.8; N, 9.6; M (cryoscopy in benzene) 1 322. Calc. for $C_{60}H_{120}Mn_6N_{12}O_{24}$: C, 41.8; H, 7.0; N, 9.8%; M 1 723]. Magnetic susceptibility at 293 K: $\chi_M^{corr.}$ = 1.946 × 10^{-7} m^3 mol^{-1} (diamagnetic correction = −1.96 × 10^{-9} m^3 mol^{-1}), corresponding to $\mu_{eff.}$ = 6.00.

X-*Ray Data collection and Refinement for Compound* (**3**).—A tabular pale pink crystal with dimensions 0.25 × 0.18 × 0.10 mm sealed in a glass capillary was mounted on the diffractometer, as for the other compound. The crystals are monoclinic. From systematic extinctions the space groups Cc or $C2/c$ were regarded as possible.

Crystal data. $C_{60}H_{120}Mn_6N_{12}O_{24}$, M = 1 722.6, a = 18.546(3), b = 19.287(3), c = 24.877(3) Å, β = 95.38(2)°, U = 8 859.2 Å^3 (*cf.* the analogous cobalt compound:[1c] the symmetry and the cell dimensions show that the two compounds are isostructural); Z = 4, D_c = 1.290 g cm^{-3}, μ = 9.1 cm^{-1}.

A total of 7 990 $\pm h \pm kl$ reflections were measured and merged to give 4 250 independent reflections, of which 1 478 having $I > 3\sigma(I)$ were retained for the refinement of the structure. The structure was refined in the space group $C2/c$ (as used for the cobalt analogue[1c]) using the SHELX 76 package of programs,[24] starting from the atomic co-ordinates of the isostructural cobalt compound. The quantity minimized was $\Sigma w(F_o - F_c)^2$. Because of the unfavourable ratio of the number of observations to the number of parameters, anisotropic thermal parameters were refined only for the Mn atoms. The high values reached by the parameters of some C atoms belonging to the terminal ethyl chains are indicative of strong thermal motion or, more probably, of some positional disorder. This is also the cause of some unrealistic C–C bond distances found in the ethyl chains of the carbamato ligand. A similar orientational disorder was observed in the cobalt compound.[1c]

Table 2. Fractional atomic co-ordinates in $[Mn_6(O_2CNEt_2)_{12}]$. Estimated standard deviations in parentheses refer to the last digit

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mn(1)	−0.042 6(2)	0.276 6(2)	0.833 3(1)	C(6)	−0.170 2(14)	0.374 2(12)	0.855 7(10)
Mn(2)	0.041 5(2)	0.131 1(2)	0.813 8(1)	C(7)	−0.280 7(31)	0.309 2(28)	0.916 6(22)
Mn(3)	−0.084 1(2)	0.421 8(2)	0.770 0(1)	C(8)	−0.227 5(26)	0.345 7(25)	0.944 8(20)
O(1)	−0.006 4(8)	0.234 3(8)	0.907 6(6)	C(9)	−0.292 6(19)	0.433 5(18)	0.870 8(14)
O(2)	0.053 6(8)	0.134 6(8)	0.896 0(6)	C(10)	−0.263 5(27)	0.491 6(27)	0.901 1(21)
O(3)	−0.131 1(8)	0.322 3(8)	0.866 9(6)	C(11)	−0.107 0(12)	0.276 6(11)	0.712 2(9)
O(4)	−0.164 0(8)	0.418 5(8)	0.820 5(6)	C(12)	−0.199 4(23)	0.230 1(21)	0.628 8(17)
O(5)	−0.061 2(7)	0.242 7(6)	0.690 2(5)	C(13)	−0.192 3(29)	0.263 5(26)	0.606 6(21)
O(6)	−0.098 1(6)	0.310 3(6)	0.754 9(5)	C(14)	−0.235 3(16)	0.321 6(15)	0.710 0(12)
O(7)	0.067 9(7)	0.168 4(6)	0.695 7(5)	C(15)	−0.267 6(16)	0.276 7(15)	0.751 5(12)
O(8)	0.127 6(8)	0.118 0(7)	0.767 8(6)	C(16)	0.123 3(13)	0.133 0(12)	0.719 6(10)
O(9)	−0.002 9(7)	0.384 6(6)	0.673 8(5)	C(17)	0.247 1(19)	0.082 6(19)	0.714 7(14)
O(10)	−0.106 9(8)	0.436 5(8)	0.688 1(6)	C(18)	0.220 4(21)	0.016 8(23)	0.713 0(17)
O(11)	0.004 9(10)	0.029 5(9)	0.795 1(8)	C(19)	0.171 5(16)	0.135 0(15)	0.630 4(12)
O(12)	−0.041 6(9)	0.521 7(8)	0.778 4(7)	C(20)	0.131 6(20)	0.078 5(18)	0.593 3(15)
N(1)	0.043 1(12)	0.171 8(12)	0.979 3(10)	C(21)	−0.061 0(12)	0.418 0(11)	0.658 3(9)
N(2)	−0.229 3(13)	0.382 8(11)	0.885 9(9)	C(22)	−0.013 0(16)	0.422 2(15)	0.567 0(12)
N(3)	−0.176 7(11)	0.278 0(10)	0.688 6(8)	C(23)	0.044 6(19)	0.475 5(18)	0.570 3(14)
N(4)	0.174 5(13)	0.115 2(11)	0.688 0(10)	C(24)	−0.147 6(17)	0.467 9(18)	0.579 6(13)
N(5)	−0.069 1(11)	0.438 5(10)	0.604 9(9)	C(25)	−0.122 0(27)	0.533 0(28)	0.587 3(20)
N(6)	0.0000	−0.070 4(16)	0.7500	C(26)	0.0000	0.005 0(24)	0.7500
N(7)	0.0000	0.623 8(17)	0.7500	C(27)	−0.012 0(18)	−0.110 6(15)	0.698 2(12)
C(1)	0.028 3(15)	0.180 6(15)	0.924 3(12)	C(28)	0.058 6(22)	−0.121 2(19)	0.677 2(15)
C(2)	0.066 1(24)	0.098 4(21)	1.002 8(17)	C(29)	0.0000	0.549 0(22)	0.7500
C(3)	0.134 8(34)	0.114 8(30)	1.011 6(24)	C(30)	−0.057 3(18)	0.660 4(16)	0.778 5(13)
C(4)	0.021 9(22)	0.235 3(19)	1.017 8(15)	C(31)	−0.019 6(20)	0.669 0(20)	0.830 4(16)
C(5)	−0.051 6(43)	0.206 4(39)	1.020 5(29)				

No hydrogen contribution was included: the refinement converged to *R*(unweighted) = 0.078 and R' = 0.085 $\{w = \Sigma[\sigma^2(F_o) + 0.1017F_o^2]^{-1}\}$ for 220 parameters and 1 478 observed reflections. No extinction coefficient was applied.

The atomic scattering factors were taken from ref. 24 for C, N, and O, and from ref. 25 for Mn; a correction for anomalous dispersion was included. The atomic co-ordinates are listed in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Synthesis of $[\{Mn(O_2CNPr^i_2)_2\}_n]$ (**4**).—This compound was prepared in a manner analogous to that reported for (**2**). Starting from $[Mn(cp)_2]$ (2.47 g, 13.3 mmol) and $NHPr^i_2$ (2.72 g, 26.9 mmol) in toluene (100 cm^3) under CO_2, 2.87 g of compound (**4**) were obtained (63% yield). Attempts at recrystallization failed due to the high solubility of this product, even in aliphatic hydrocarbons (Found: C, 48.8; H, 8.0; N, 8.1. Calc. for $C_{14}H_{28}MnN_2O_4$: C, 49.0; H, 8.2; N, 8.1%).

Reaction of Compound (**3**) *with Sodium*.—To a suspension of sodium sand (0.32 g, 13.9 mmol) in thf (30 cm^3) was added compound (**3**) (1.710 g, 5.9 mmol). The clear suspension slowly became black and a solid began to precipitate. After 10 d it was filtered off and dried *in vacuo*, leaving 1.69 g of a grey, pyrophoric material, probably containing metallic manganese. It can be dissolved in aqueous acids or neutral water with rapid gas evolution and formation of colourless solutions. Its i.r. spectrum as a Nujol mull was superimposable upon that of an authentic sample of $Na(O_2CNEt_2)$, prepared from $NHEt_2$, CO_2 and sodium sand.[26]

Reaction of Compound (**4**) *with* PhCOCl.—Compound (**4**) (0.27 g, 0.8 mmol) was dissolved in n-heptane (25 cm^3), and PhCOCl (0.23 g, 1.6 mmol) was added. The formation of a light brown solid was observed. Infrared analysis of the liquid phase showed the disappearance of the starting compound and the presence of two bands at 1 780 and 1 730 cm^{-1}, due to $PhC(O)OC(O)NPr^i_2$.[2]

Reaction of Compound (**3**) *with Electrophiles*.—(*a*) *With* MeCOCl. A solution of compound (**3**) (0.48 g, 1.7 mmol) in thf (50 cm^3) was treated with MeCOCl (0.26 g, 3.3 mmol). After 2 h a colourless solid was present, and the i.r. spectrum of the liquid phase showed the disappearance of the starting compounds and the presence of two bands at 1 790 and 1 740 cm^{-1}, attributed to the mixed anhydride $MeC(O)OC(O)NEt_2$. After 24 h the solid had totally disappeared and the i.r. spectrum of the yellow clear solution showed the presence of CO_2 (2 340 cm^{-1}) and $MeC(O)NEt_2$, both free ($\tilde{\nu}_{CO}$ = 1 640 cm^{-1}) and bonded to $MnCl_2$ ($\tilde{\nu}_{CO}$ = 1 595 cm^{-1}), as confirmed by the spectrum of the solution obtained by adding the amide to a suspension of $MnCl_2$ in thf.

(*b*) *With* $SiMe_3Cl$. To a solution of compound (**3**) (0.98 g, 3.4 mmol) in thf (25 cm^3) was added $SiMe_3Cl$ (1.5 cm^3, 11.9 mmol), and the mixture was stirred for 15 h. During this time a colourless solid precipitated and the i.r. spectrum of the final solution in the carbonyl stretching region consisted of only one strong band at 1 690 cm^{-1}. The solid was separated by filtration and its i.r. spectrum as a Nujol mull was consistent with the formulation $[MnCl_2(thf)_2]$ (81% yield).[27] The solvent was evaporated under reduced pressure, to leave about 1 cm^3 of liquid. After warming at 40 °C at 0.1 mmHg, 0.90 g of a colourless, extremely moisture sensitive, liquid was collected in a cold trap. The i.r. spectrum of this liquid was identical with that of an authentic sample of $Et_2NCOOSiMe_3$[28] (70% yield).

(*c*) *With* $[\{Ti(cp)_2Cl\}_2]$.—The compound $[\{Ti(cp)_2Cl\}_2]$ (0.85 g, 2.0 mmol) was suspended in toluene (50 cm^3), and compound (**3**) (0.56 g, 1.95 mmol) was added. The colour of the suspension changed immediately to bright green and after 30 min the suspended solid was filtered off and the solution evaporated to dryness. A green oil was obtained, which dissolved in n-heptane (25 cm^3) to give a blue solution. A small amount of a yellow solid was eliminated by filtration and the solution cooled to −80 °C. After 5 d, beautiful blue needles (0.70 g) were collected by rapid filtration of the cold solution (61% yield) [Found: Ti, 16.25; *M* (cryoscopy in benzene) 289. Calc. for $C_{15}H_{20}NO_2Ti$: Ti, 16.30%; *M* 294]. Magnetic susceptibility at 297 K: $\chi_M^{corr.} = 1.46 \times 10^{-8}$ m^3 mol^{-1} (diamagnetic correction = -2.19×10^{-9} m^3 mol^{-1}), corresponding to $\mu_{eff.} = 1.66$. The same product was synthesized as described below.

Synthesis of $[Ti(cp)_2(O_2CNEt_2)]$ *from* $[\{Ti(cp)_2Cl\}_2]$, $NHEt_2$, *and* CO_2.—A solution of $NHEt_2$ (0.5 cm^3, 4.8 mmol) in toluene (15 cm^3) was saturated with CO_2, and $[\{Ti(cp)_2Cl\}_2]$ (0.27 g, 0.6 mmol) was added. The solution became blue and a colourless solid precipitated. After 2 h this solid was filtered off and the solution evaporated to dryness. The blue residue was taken up in n-heptane (10 cm^3) and, after cooling at −80 °C for 3 d, blue needles of the product (0.29 g) were obtained (52% yield), whose i.r. spectrum was identical with that of the same compound obtained from (**3**).

Reactions with MeI.—(*a*) A thf solution (10 cm^3) of compound (**3**) (0.53 g, 1.8 mmol) was treated with MeI (4.56 g, 32.1 mmol) for 15 h. A yellow, fluorescent solid, containing some tetra-alkylammonium iodide, separated slowly from the solution, and was collected by filtration and dried (0.83 g) (Found: C, 19.7; H, 4.4; I, 65.6; N, 3.8. Calc. for $C_{13.8}H_{36.8}I_{4.3}MnN_{2.3}$: C, 19.9; H, 4.4; I, 65.3; N, 3.8%). These data correspond to the chemical composition $[NMe_2Et_2]_2[MnI_4]\cdot0.3NMe_2Et_2I$. The mother solution was found by i.r. spectroscopy to contain CO_2 and some unreacted carbamate.

(*b*) An analogous reaction between compound (**4**) (0.38 g, 1.1 mmol) and MeI (2.28 g, 16.1 mmol) in thf (10 cm^3) gave a yellow fluorescent solid (0.32 g), containing some tetra-alkylammonium iodide (Found: C, 26.4; H, 5.6; I, 57.5; N, 3.9. Calc. for $C_{26.4}H_{66.0}I_{5.3}MnN_{3.3}$: C, 27.4; H, 5.7; I, 58.2; N, 4.0%). These data correspond to the chemical composition $[NMe_2Pr^i{}_2]_2[MnI_4]\cdot1.3NMe_2Pr^i{}_2I$. Carbon dioxide and some unreacted carbamate were detected in the mother solution by i.r. spectroscopy.

Reaction of Compound (**3**) *with Dimethyl Sulphate.*—A thf solution (25 cm^3) of compound (**3**) (0.26 g, 0.9 mmol) was treated with Me_2SO_4 (0.5 cm^3, 5.3 mmol). A colourless solid slowly precipitated, accompanied by gas evolution. After 16 h the i.r. spectrum of the solution no longer showed the bands of the starting carbamate, nor any other absorption in the carbonyl stretching region. The colourless solid was collected by filtration and dried (0.50 g). Its i.r. spectrum clearly showed strong bands between 1 300 and 1 000 cm^{-1} due to the sulphate group. This solid (0.22 g) was dissolved in D_2O (1 cm^3) and a spatula end of Na_2CO_3 was added in order to remove Mn^{2+} from the solution. The suspension was filtered and its ^1H n.m.r. spectrum showed the following resonances (δ, multiplicity, relative intensity): 3.8, s, 3 H (Me_2SO_4); 2.3, q, 2 H; 3.1, s, 3 H; 1.5, t, 3 H; as expected for the $NMe_2Et_2{}^+$ ion. Evaporation of the mother-liquor left only a few drops of a colourless liquid identified as unreacted Me_2SO_4 by its i.r. spectrum.

Acknowledgements

The authors thank the Consiglio Nazionale delle Ricerche (C.N.R., Roma), Progetto Finalizzato Energetica II for financial support, and the Ente Nazionale Idrocarburi (ENI, Roma) for a fellowship (to A. B.).

References

1 (*a*) F. Calderazzo, G. Dell'Amico, R. Netti, and M. Pasquali, *Inorg. Chem.*, 1978, **17**, 471; (*b*) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, and G. Perego, *J. Chem. Soc., Dalton Trans.*, 1983, 483; (*c*) D. Belli Dell'Amico, F. Calderazzo, B. Giovannitti, and G. Pelizzi, *ibid.*, 1984, 647; (*d*) F. Calderazzo, D. Belli Dell'Amico, and G. Pelizzi, *Gazz. Chim. Ital.*, 1985, **115**, 145; (*e*) D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, and G. Pelizzi, *ibid.*, 1986, **116**, 609; (*f*) D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, and G. Pelizzi, *Chem. Ber.*, 1987, **120**, 955; (*g*) E. Agostinelli, D. Belli Dell'Amico, F. Calderazzo, D. Fiorani, and G. Pelizzi, *Gazz. Chim. Ital.*, in the press.

2 D. Belli Dell'Amico, F. Calderazzo, and U. Giurlani, *J. Chem. Soc. Chem. Commun.*, 1986, 1000.

3 (*a*) R. P. A. Sneeden in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, E. W. Abel, and F. G. A. Stone, Pergamon, Oxford, 1981, vol. 8, p. 225; (*b*) D. J. Darensbourg and R. A. Kudaroski, *Adv. Organomet. Chem.*, 1983, **22**, 129; (*c*) A. L. Lapidus and Y. Y. Ping, *Russ. Chem. Rev.*, 1981, **50**, 63.

4 (*a*) F. Lynen, J. Knappe, E. Lorch, G. Jütting, and E. Ringelmann, *Angew. Chem.*, 1959, **71**, 481; (*b*) M. J. Cravey and H. Kohn, *J. Am. Chem. Soc.*, 1980, **102**, 3928; (*c*) G. R. J. Thatcher, R. Poirier, and R. Kluger, *ibid.*, 1986, **108**, 2699.

5 J. A. Leigh, K. L. Rinehart, and R. S. Wolfe, *Biochemistry*, 1985, **24**, 995.

6 (*a*) G. H. Lorimer, *Annu. Rev. Plant. Physiol.*, 1981, **32**, 349; (*b*) S. Styring and R. Bränden, *Biochemistry*, 1985, **24**, 6011; (*c*) H. M. Miziorko and R. C. Sealy, *ibid.*, 1980, **19**, 1167.

7 A. S. Mildvan and M. C. Scrutton, *Biochemistry*, 1967, **6**, 2978.

8 T. Tsuda, Y. Chujo, T. Hayasaki, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1979, 797.

9 G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, 1956, **2**, 95.

10 J. Heck, W. Massa, and P. Weinig, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 722.

11 C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1984, **106**, 2033.

12 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Wiley, New York, 1966, p. 45.

13 J. Delaunay and R. P. Hugel, *Inorg. Chem.*, 1986, **25**, 3957.

14 F. L. Phillips, F. M. Shreeve, and A. C. Skapski, *Acta Crystallogr., Sect. B*, 1976, **32**, 687.

15 A. R. E. Baikie, A. J. Howes, M. B. Hursthouse, A. B. Quick, and P. Thornton, *J. Chem. Soc., Chem. Commun.*, 1986, 1587.

16 F. Calderazzo, G. Dell'Amico, M. Pasquali, and G. Perego, *Inorg. Chem.*, 1978, **17**, 474.

17 S. J. O'Keefe and J. R. Knowles, *J. Am. Chem. Soc.*, 1986, **108**, 328.

18 R. S. P. Coutts and P. C. Wailes, *Aust. J. Chem.*, 1967, **20**, 1579.

19 R. S. P. Coutts and P. C. Wailes, *Chem. Commun.*, 1968, 1170.

20 T. Tsuda, H. Washita, K. Watanabe, M. Miwa, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1978, 815.

21 Y. Yoshida, S. Ishii, and T. Yamashita, *Chem. Lett.*, 1984, 1571.

22 J. H. Huheey, 'Inorganic Chemistry,' 2nd edn., Harper and Row, New York, 1972, appendix F.

23 L. E. Manzer, *J. Organomet. Chem.*, 1976, **110**, 291.

24 G. M. Sheldrick, SHELX 76, a program for crystal structure determination, University of Cambridge, 1976.

25 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101.

26 U. Giurlani, Tesi di Laurea in Chimica, Pisa, 1986.

27 R. J. Kern, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1105.

28 G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, 1964, **97**, 891.

Received 23rd December 1987; *Paper* 7/2248