DALTON

Polynuclear aggregation of cobalt and manganese dichlorides. Synthesis, properties and structures of monomeric [$CoCl_2$(tmen)], ionic [$Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3$(tmen)$_3$][$BPh_4$], polymeric $MnCl_2$·tmen and tetranuclear [$Mn_4(\mu\text{-}Cl)_6Cl_2$(tmen)$_4$] (tmen = $Me_2NCH_2CH_2NMe_2$)†

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The complexes [$CoCl_2$(tmen)] **1**, [$Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3$(tmen)$_3$][$BPh_4$]·[$CoCl_2$(tmen)] **2**, $MnCl_2$·tmen **3** and [$Mn_4(\mu\text{-}Cl)_6Cl_2$(tmen)$_4$] **4** (tmen = $Me_2NCH_2CH_2NMe_2$) have been synthesized and structurally characterized by X-ray diffraction. The crystals of **1** consist of the tetrahedral [$CoCl_2$(tmen)] molecules. The structure of the co-crystallite **2** is composed of two independent species, ionic [$Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3$(tmen)$_3$][$BPh_4$] and molecular [$CoCl_2$(tmen)]. In the first compound the trinuclear [$Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3$(tmen)$_3$]$^+$ cations consist of *triangulo*-{Co_3Cl_3} units defined by three cobalt atoms with three bridging chloride atoms in the same plane. The remaining two μ_3-chloride atoms are symmetrically placed above and below the molecular plane. The polymeric chain of compound **3** is formed by six-co-ordinate manganese(II) centres linked by double chloride bridges. Two nitrogen atoms from the co-ordinated tmen complete the octahedral co-ordination of the manganese. The crystals of compound **4** consist of tetranuclear molecules in which two internal six-co-ordinate and two peripheral five-co-ordinate Mn atoms are linked by double chloride bridges. The natures of the ligand and solvent as key factors promoting the particular aggregation of the cobalt and manganese dichlorides is discussed.

The chemistry of the first-row transition-metal(II) compounds containing chlorides and tetrahydrofuran (thf) is not well known yet. Metal dichlorides (M = Mn, Fe, Co or Ni) form with thf compounds of composition $MCl_2(thf)_{1.5}$.[1] X-Ray diffraction studies showed the iron and cobalt compounds to be tetranuclear [$M_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6$] (M = Fe[2] or Co[3]). These species contain two types of metal centres: six- and five-co-ordinate atoms bridged by two μ_3- and four μ-chloride atoms. However, the tendency of the metal(III) compounds to lose one thf molecule in less-polar solvents, *e.g.* CH_2Cl_2 and form dimeric [$M_2(\mu\text{-}Cl)_2Cl_4(thf)_4$] (M = Ti[4] or V[5]) complexes has prompted us to attempt to create new cobalt(II) and manganese(II) species either molecular or ionic. Substitution of thf by $Me_2NCH_2CH_2NMe_2$ (tmen) molecules in both molecular and cationic species seems to be a convenient route to unusual geometries.[6] The properties and nature of these compounds are especially attractive, in the absence of a direct metal–metal bond, for studying the factors which favour polynuclear aggregation in both the solid state and solution. Moreover interest in the chemistry of cobalt(II) compounds including chloride and thf has also been stimulated by the search for new olefin-polymerization catalytic precursors since the recently reported use of simple cobalt salts in combination with AlR_3 to give high-molecular-weight pure all-*cis*-poly(norbornene)[7] (norbornene = bicyclo[2.2.1]hept-2-ene).

We described here the synthesis and crystallographic study of monomeric [$CoCl_2$(tmen)] **1**, ionic [$Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3$(tmen)$_3$][$BPh_4$] **2**, polymeric $MnCl_2$·tmen **3** and tetrameric [$Mn_4(\mu\text{-}Cl)_6Cl_2$(tmen)$_4$] **4** compounds.

Results and Discussion

Synthesis and structure of [$CoCl_2$(tmen)] 1

The blue crystalline air-sensitive product **1** was obtained from the reaction of $CoCl_2$·1.5thf with tmen in CH_2Cl_2 under dinitrogen. It is paramagnetic with μ_{eff} 4.83 μ_B, consistent with tetrahedral cobalt(II). The IR spectrum contained bands at 319s and 350vs and 441w, 472w and 501w cm^{-1} assigned to ν(Co–Cl) and ν(Co–N) vibrations, respectively. The electronic spectrum in dichloromethane solution shows bands at 15 151, 17 316 and 19 047 cm^{-1} as the result of splitting of the $^4A_2 \longrightarrow {}^4T_1(P)$ transition, similar to those observed for tetrahedral high-spin d^7 compounds, *e.g.* [NBu_4]$_2$[$CoCl_4$].[8] The elemental analysis, IR and electronic spectra suggested a tetrahedral molecular species. This was confirmed by an X-ray structural study.

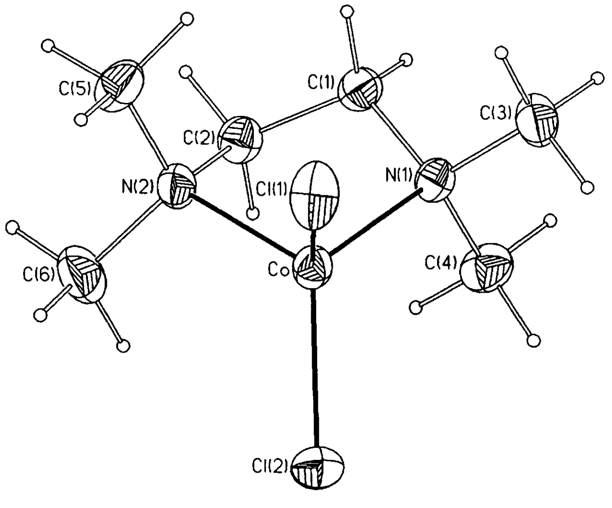

Fig. 1 Structure and numbering scheme of complex **1**

Crystalline dichloro(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)cobalt(II) is composed of discrete monomeric, four-co-ordinate molecules. Its structure is depicted in Fig. 1 and selected bond distances and angles are listed in Table 1. The cobalt atom is surrounded by two chloride atoms and two nitrogen atoms from the chelate tmen ligand and exhibits

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Co–N(1)	2.081(3)	Co–N(2)	2.073(3)
Co–Cl(1)	2.218(1)	Co–Cl(2)	2.218(1)
N(1)–C(1)	1.478(4)	N(2)–C(2)	1.483(4)
N(1)–C(3)	1.484(5)	N(2)–C(5)	1.475(5)
N(1)–C(4)	1.479(4)	N(2)–C(6)	1.482(5)
C(1)–C(2)	1.502(5)		
Cl(1)–Co–Cl(2)	117.5(1)	Cl(2)–Co–N(1)	111.8(1)
Cl(1)–Co–N(1)	113.1(1)	Cl(2)–Co–N(2)	111.8(1)
Cl(1)–Co–N(2)	111.4(1)	N(1)–Co–N(2)	87.6(2)
Co–N(1)–C(1)–C(2)	108.5(5)	N(1)–C(1)–C(2)–N(2)	−75.1(5)
Co–N(2)–C(2)–C(1)	11.5(2)		

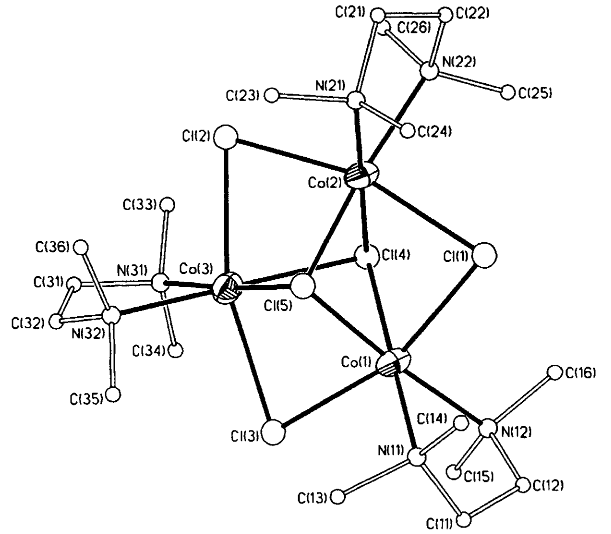

Fig. 2 Structure and numbering scheme of complex **2** (H atoms omitted for clarity)

tetrahedral co-ordination. The cobalt atom and the chelate ligand form a five-membered ring. The molecule as a whole possesses pseudo-C_2 symmetry. The tetrahedron around cobalt is somewhat distorted, especially the N(1)–Co–N(2) angle which is only 87.6(2)°. This angle is a little bit smaller than the corresponding one in dichloro(*N*,*N*′-ethylenedimorpholine)cobalt(II),[9] 88.9(4)°, but still greater that those in other MCl_2 complexes with unsubstituted ethane-1,2-diamine, $[Cu(en)_2(NO_3)_2]$[10] has a N–Cu–N angle of 86.2°. The Co–Cl and Co–N bond distances (see Table 1) are similar to those found in Cs_3CoCl_5,[11] Cs_2CoCl_4,[12] dichloro(*N*,*N*′-ethylenedimorpholine)cobalt(II),[9] dichloro(*p*-toluidine)cobalt(II)[13] and dichloro(*N*,*N*,*N*′,*N*′-tetraethylethane-1,2-diamine)cobalt(II).[14]

Synthesis and structure of $[Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(tmen)_3][BPh_4]\cdot[CoCl_2(tmen)]$ 2

The reaction of complex **1** with $NaBPh_4$ in thf formed a blue solution from which blue-violet crystals of $[Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(tmen)_3][BPh_4]\cdot[CoCl_2(tmen)]$ **2** were isolated, equation (1). The structure of the co-crystallite **2** is composed of two

$$4[CoCl_2(tmen)] + NaBPh_4 \xrightarrow{thf} [Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(tmen)_3][BPh_4]\cdot[CoCl_2(tmen)] + NaCl \quad (1)$$

independent $[Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(tmen)_3][BPh_4]$ and $[CoCl_2(tmen)]$ molecules. The first species consist of trinuclear $[Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(tmen)_3]^+$ cations and BPh_4^- anions in a 1 : 1 ratio.

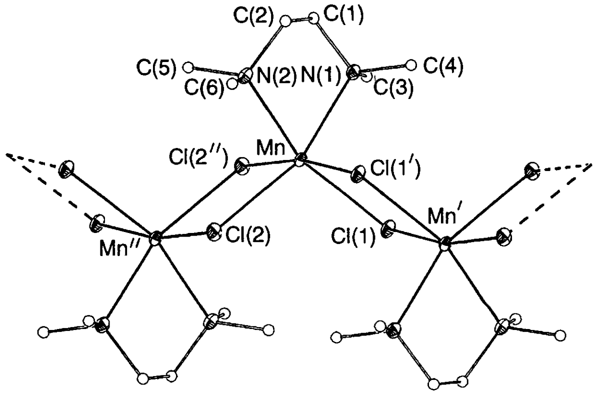

Fig. 3 Structure and numbering scheme of complex **3** (H atoms omitted for clarity)

Its overall view is shown in Fig. 2 with selected bond lengths and angles in Table 2. In the cation the geometry of the *triangulo*-$\{Co_3Cl_3\}$ unit is defined by three cobalt atoms with three bridging chloride atoms in the same plane, the remaining two μ_3-chloride atoms being symmetrically placed above and below the molecular plane. Each of the three molecules of tmen chelates one of the three equivalent cobalt atoms, imposing a slightly distorted octahedral geometry on each metal centre. The Co–(μ-Cl) and Co–(μ_3-Cl) bond distances (see Table 2), formed by the equatorial and apical chloride atoms, are comparable to μ *vs.* μ_3 in $[Co_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$.[3] No special features were observed for the three tmen molecules. The structure of the cobalt cation is identical to those of Ti^{II}[15] and V^{II}[15,16] in $[M_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_2(tmen)_3]^+$. The tetraphenylborate counter ions possess a geometry close to ideal tetrahedral; the observed bond lengths and angles are similar to those previously observed for the same anion, *e.g.* in benzoyltriethylammonium tetraphenylborate.[17]

The second molecule is the monomeric $[CoCl_2(tmen)]$ complex identical to complex **1** the geometry of which is described above. All the bond angles and distances are analogous in the range of standard deviations (see Table 2).

Synthesis and structure of $MnCl_2\cdot$tmen 3

The reaction of $MnCl_2$ with a stoichiometric amount of tmen in tetrahydrofuran gives air-sensitive colourless crystals of composition $MnCl_2\cdot$tmen **3**, which can be stored under N_2. The crystalline species has good solubility in thf, but is unstable, undergoing decomposition, on exposure either to air or moisture to give unidentified products. The IR spectrum shows bands at 209vs and 442s, 455m and 476s cm^{-1} assigned to ν(Mn–Cl) and ν(Mn–N), respectively.

In contrast to the monomeric cobalt compound **1**, $MnCl_2\cdot$tmen **3** in the crystalline state is a linear polymer. Its overall view and the numbering scheme are shown in Fig. 3, selected bond lengths, angles and torsion angles in Table 3. Species **3** consists of six-co-ordinate manganese(II) centres linked by double chloride bridges to form a polymeric chain. Two nitrogen atoms from the co-ordinated tmen molecule (in *cis* position) complete the octahedral co-ordination sphere. The octahedron is distorted due to the chelating character of tmen (see Table 3). The Mn–Cl bond distances range from 2.536(1) to 2.608(1) Å and are generally similar to the Mn^{II}–Cl bond lengths observed in other octahedral manganese(II) compounds.[18] The Mn–N(1) and Mn–N(2) distances of 2.362(2) and 2.360(2) Å are also typical. The temperature-independent (80–293 K) magnetic moment μ_{eff} = 5.89 μ_B per Mn atom (linear plot of $1/\chi$ against T passing through the origin) is consistent with non-interacting high-spin d^5 centres and is similar to those found for other compounds $MnCl_2\cdot A$ (A = diamine),[19] not structurally characterized, but for which linear polymeric structures have been suggested.

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **2**

Co(1)–Cl(1)	2.470(3)	Co(2)–Cl(2)	2.439(3)	Co(3)–Cl(3)	2.461(3)	Co(4)–N(21)	2.108(13)
Co(1)–Cl(3)	2.484(4)	Co(2)–Cl(4)	2.572(3)	Co(3)–Cl(4)	2.565(3)	Co(4)–N(22)	2.059(12)
Co(1)–Cl(4)	2.567(3)	Co(2)–Cl(5)	2.078(6)	Co(3)–Cl(5)	2.047(8)	B–C(100)	1.640(14)
Co(1)–Cl(5)	2.084(6)	Co(2)–N(21)	2.158(10)	Co(3)–N(31)	2.079(10)	B–C(200)	1.655(15)
Co(1)–N(11)	2.183(11)	Co(2)–N(22)	2.166(11)	Co(3)–N(32)	2.160(10)	B–C(300)	1.633(14)
Co(1)–N(12)	2.165(10)	Co(3)–Cl(2)	2.460(3)	Co(4)–Cl(6)	2.204(4)	B–C(400)	1.590(16)
Co(2)–Cl(1)	2.448(3)			Co(4)–Cl(7)	2.156(4)		
Cl(1)–Co(1)–Cl(3)	162.0(2)	Cl(5)–Co(1)–N(12)	170.8(4)	Cl(4)–Co(2)–N(22)	94.9(3)	Cl(4)–Co(3)–Cl(5)	77.2(3)
Cl(1)–Co(1)–Cl(4)	84.8(1)	N(11)–Co(1)–N(12)	83.6(4)	Cl(5)–Co(2)–N(21)	106.5(4)	Cl(4)–Co(3)–N(31)	96.9(3)
Cl(1)–Co(1)–Cl(5)	82.1(3)	Cl(1)–Co(2)–Cl(2)	162.8(2)	Cl(5)–Co(2)–N(22)	171.2(4)	Cl(4)–Co(3)–N(32)	178.8(4)
Cl(1)–Co(1)–N(11)	96.8(4)	Cl(1)–Co(2)–Cl(4)	85.2(1)	N(21)–Co(2)–N(22)	82.2(4)	Cl(5)–Co(3)–N(31)	173.8(4)
Cl(1)–Co(1)–N(12)	96.3(3)	Cl(1)–Co(2)–Cl(5)	82.8(3)	Cl(2)–Co(3)–Cl(3)	162.2(2)	Cl(5)–Co(3)–N(32)	101.8(4)
Cl(3)–Co(1)–Cl(4)	83.0(1)	Cl(1)–Co(2)–N(21)	97.3(3)	Cl(2)–Co(3)–Cl(4)	82.8(1)	N(31)–Co(3)–N(32)	84.2(5)
Cl(3)–Co(1)–Cl(5)	82.2(3)	Cl(1)–Co(2)–N(22)	94.6(3)	Cl(2)–Co(3)–Cl(5)	82.4(3)	Cl(6)–Co(4)–Cl(7)	114.4(2)
Cl(3)–Co(1)–N(11)	95.8(4)	Cl(2)–Co(2)–Cl(4)	83.1(1)	Cl(2)–Co(3)–N(31)	95.1(3)	Cl(6)–Co(4)–N(41)	114.8(4)
Cl(3)–Co(1)–N(12)	97.7(3)	Cl(2)–Co(2)–Cl(5)	82.3(3)	Cl(2)–Co(3)–N(32)	97.7(4)	Cl(6)–Co(4)–N(42)	114.3(4)
Cl(4)–Co(1)–Cl(5)	76.5(3)	Cl(2)–Co(2)–N(21)	95.1(3)	Cl(3)–Co(3)–Cl(4)	83.5(1)	Cl(7)–Co(4)–N(41)	116.0(4)
Cl(4)–Co(1)–N(11)	177.5(4)	Cl(2)–Co(2)–N(22)	98.9(3)	Cl(3)–Co(3)–Cl(5)	83.5(3)	Cl(7)–Co(4)–N(42)	107.4(4)
Cl(4)–Co(1)–N(12)	94.3(3)	Cl(4)–Co(2)–Cl(5)	76.5(3)	Cl(3)–Co(3)–N(31)	97.8(3)	N(41)–Co(4)–N(42)	86.6(5)
Cl(5)–Co(1)–N(11)	105.6(4)	Cl(4)–Co(2)–N(21)	176.3(3)	Cl(3)–Co(3)–N(32)	95.8(4)		
Co(1)–Cl(1)–Co(2)	77.6(1)	Co(1)–Cl(4)–Co(2)	73.7(1)	Co(2)–Cl(4)–Co(3)	73.9(1)	Co(1)–Cl(5)–Co(3)	96.6(3)
Co(2)–Cl(2)–Co(3)	78.1(1)	Co(1)–Cl(4)–Co(3)	73.9(1)	Co(1)–Cl(5)–Co(2)	95.5(3)	Co(2)–Cl(5)–Co(3)	96.9(3)
Co(1)–Cl(3)–Co(3)	77.2(1)						

Table 3 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for complex **3**

$Mn\cdots Mn'$	3.941(1)	$Mn\cdots Mn''$	3.940(1)
Mn–Cl(1)	2.536(1)	Mn–Cl(2)	2.543(1)
Mn–Cl(1′)	2.608(1)	Mn–Cl(2″)	2.600(1)
Mn–N(1)	2.362(2)	Mn–N(2)	2.360(2)
N(1)–C(1)	1.479(4)	N(2)–C(2)	1.473(4)
N(1)–C(3)	1.479(4)	N(2)–C(5)	1.458(5)
N(1)–C(4)	1.452(5)	N(2)–C(6)	1.473(4)
C(1)–C(2)	1.491(4)		
Cl(1)–Mn–Cl(1′)	80.0(1)	Cl(2)–Mn–N(1)	161.4(1)
Cl(1)–Mn–Cl(2)	106.5(1)	Cl(2)–Mn–N(2)	89.6(1)
Cl(1)–Mn–Cl(2″)	93.7(1)	Cl(2″)–Mn–N(1)	89.4(1)
Cl(1)–Mn–N(1)	89.3(1)	Cl(2″)–Mn–N(2)	99.0(1)
Cl(1)–Mn–N(2)	161.1(1)	N(1)–Mn–N(2)	76.9(1)
Cl(1′)–Mn–Cl(2)	94.1(1)	Mn–Cl(1)–Mn′	100.0(1)
Cl(1′)–Mn–Cl(2″)	169.9(1)	Mn–Cl(2)–Mn″	100.0(1)
Cl(1′)–Mn–N(1)	98.3(1)	Mn–N(1)–C(1)	106.0(2)
Cl(1′)–Mn–N(2)	89.2(1)	Mn–N(2)–C(2)	106.7(2)
Mn–N(1)–C(1)–C(2)	−43.6(3)	N(1)–C(1)–C(2)–N(2)	61.7(4)
Mn–N(2)–C(2)–C(1)	−43.0(3)		

Primed atoms are related to unprimed by $-x$, $-y$, $-z$, doubly primed atoms by $1 - x$, $-y$, $-z$.

Synthesis and structure of $[Mn_4(\mu\text{-}Cl)_6Cl_2(tmen)_4]$ 4

Reaction of $MnCl_2$ and tmen in CH_2Cl_2 gave colourless needle-shaped crystals. X-Ray structural analysis showed them to be tetranuclear $[Mn_4(\mu\text{-}Cl)_6Cl_2(tmen)_4]$ as shown in Fig. 4. Selected bond lengths, angles and torsion angles are presented in Table 4. Crystals of **4** consist of discrete $[Mn_4Cl_2(\mu\text{-}Cl)_6(tmen)_4]$ molecules. The structure includes two internal six- and two peripheral five-co-ordinated manganese(II) centres linked by double chloride bridges to form a tetranuclear species with a symmetry centre. Two nitrogen atoms from one tmen molecule complete the co-ordination sphere of each internal Mn^{II}. For the peripheral Mn atoms the five-co-ordination is completed by two nitrogen atoms from tmen and one terminal chloride atom. The $Mn(1)\cdots Mn(1')$ and $Mn(1)\cdots Mn(2)$ distances of 3.858(1) and 3.784(1) Å, respectively, are well outside those for metal–metal bonding and are similar to those found in β-$RbMnCl_3$ (3.774 Å)[20] and in $[NH_3Pr^i]_2[Mn_2(\mu\text{-}Cl)_2Cl_4(H_2O)_4]$ (3.828 Å).[21] In $[Mn_2(\mu\text{-}Cl)_2(CH_2SPh)_2\text{-}(tmen)_2]$[22] the Mn atoms are five-co-ordinated and separated by 3.806(3) Å. The $Mn\text{–}Cl_{bridge}$ distances in **4** range from 2.443(1) to 2.610(1) Å. The terminal Cl atoms are separated from peripheral manganese atoms by 2.349(1) Å. The differences in Mn–Cl bond distances are consistent with the relative *trans* influences of chloride and thf and with the differences in co-ordination mode. The bond angles around the internal as well as peripheral manganese atoms are distorted from idealized octahedral and trigonal bipyramidal, respectively, presumably due to the effect of the chelating tmen ligand. The temperature-independent magnetic moment (80–293 K) $\mu_{eff} = 5.89\ \mu_B$ per manganese atom in **4** is consistent with four non-interacting high-spin d^5 centres.

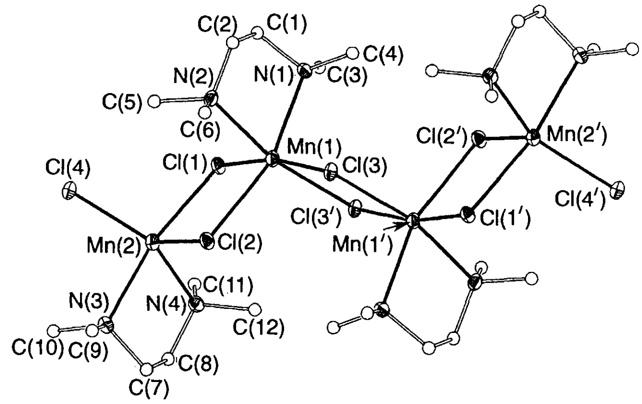

Fig. 4 Structure and numbering scheme of complex **4** (H atoms omitted for clarity)

Conclusion

The results presented show that the natures of the ligand and solvent are key factors promoting the particular aggregation of a metal dichloride. A compound of general formula $CoCl_2\cdot 1.5thf$ precipitates from thf solution as the centrosymmetric tetranuclear $[Co_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$ species,[3] in which five- and six-co-ordinated cobalt atoms are linked by two μ_3- and four μ-chloride atoms. The corresponding reaction with tmen in thf or CH_2Cl_2 led to the formation of monomeric tetrahedral compound $[CoCl_2(tmen)]$ **1**. Two different

Table 4 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for complex **4**

Mn(1) ··· Mn(1′)	3.858(1)	N(1)–C(1)	1.481(5)
Mn(1) ··· Mn(2)	3.784(1)	N(1)–C(3)	1.463(6)
Mn(1)–Cl(1)	2.542(1)	N(1)–C(4)	1.475(5)
Mn(1)–Cl(2)	2.610(1)	N(2)–C(2)	1.465(5)
Mn(1)–Cl(3)	2.536(1)	N(2)–C(5)	1.478(5)
Mn(1)–Cl(3′)	2.537(1)	N(2)–C(6)	1.471(5)
Mn(1)–N(1)	2.327(3)	N(3)–C(7)	1.476(5)
Mn(1)–N(2)	2.347(3)	N(3)–C(9)	1.463(6)
Mn(2)–Cl(1)	2.542(1)	N(3)–C(10)	1.480(6)
Mn(2)–Cl(2)	2.443(1)	N(4)–C(8)	1.478(5)
Mn(2)–Cl(4)	2.349(1)	N(4)–C(11)	1.482(5)
Mn(2)–N(3)	2.309(3)	N(4)–C(12)	1.469(4)
Mn(2)–N(4)	2.289(3)	C(1)–C(2)	1.510(6)
		C(7)–C(8)	1.497(6)
Cl(1)–Mn(1)–Cl(2)	81.7(1)	Cl(3′)–Mn(1)–N(2)	167.4(1)
Cl(1)–Mn(1)–Cl(3)	169.2(1)	N(1)–Mn(1)–N(2)	78.4(1)
Cl(1)–Mn(1)–Cl(3′)	91.5(1)	Cl(1)–Mn(2)–Cl(2)	85.1(1)
Cl(1)–Mn(1)–N(1)	89.4(1)	Cl(1)–Mn(2)–Cl(4)	96.5(1)
Cl(1)–Mn(1)–N(2)	97.0(1)	Cl(1)–Mn(2)–N(3)	167.8(1)
Cl(2)–Mn(1)–Cl(3)	92.5(1)	Cl(1)–Mn(2)–N(4)	89.6(1)
Cl(2)–Mn(1)–Cl(3′)	103.4(1)	Cl(2)–Mn(2)–Cl(4)	121.9(1)
Cl(2)–Mn(1)–N(1)	161.9(1)	Cl(2)–Mn(2)–N(3)	95.7(1)
Cl(2)–Mn(1)–N(2)	87.1(1)	Cl(2)–Mn(2)–N(4)	107.3(1)
Cl(3)–Mn(1)–Cl(3′)	81.0(1)	Cl(4)–Mn(2)–N(3)	93.4(1)
Cl(3)–Mn(1)–N(1)	98.6(1)	Cl(4)–Mn(2)–N(4)	130.8(1)
Cl(3)–Mn(1)–N(2)	91.8(1)	N(3)–Mn(2)–N(4)	78.5(2)
Cl(3′)–Mn(1)–N(1)	92.5(1)		
Mn(1)–Cl(3)–Mn(1′)	99.0(1)	Mn(1)–N(1)–C(1)	104.4(3)
Mn(1)–Cl(1)–Mn(2)	96.2(1)	Mn(1)–N(2)–C(2)	106.5(3)
Mn(1)–Cl(2)–Mn(2)	97.0(1)	Mn(2)–N(3)–C(7)	103.2(3)
		Mn(2)–N(4)–C(8)	108.3(3)
Mn(1)–N(1)–C(1)–C(2)	47.4(5)	Mn(2)–N(3)–C(5)–C(6)	−51.3(6)
Mn(1)–N(2)–C(2)–C(1)	38.6(5)	Mn(2)–N(4)–C(6)–C(5)	−32.9(6)
N(1)–C(1)–C(2)–N(2)	−61.9(6)	N(3)–C(5)–C(6)–N(4)	60.0(7)

Primed atoms are related to unprimed by $1 - x, -y, 1 - z$.

compounds **3** and **4** of common composition $MnCl_2$·tmen are produced from reactions of $MnCl_2$·1.5thf with tmen in thf and CH_2Cl_2, respectively. The compound $MnCl_2$·tmen **3** displays a polymeric nature with six-co-ordinate manganese(II) centres linked by double chloride bridges. However $[Mn_4(\mu\text{-}Cl)_6Cl_2(tmen)_4]$ **4** is a tetranuclear species with two differently co-ordinated manganese centres: five- and six-co-ordinate. Treatment of **1** with $NaBPh_4$ as chloride-abstracting agent yielded the ionic complex $[Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl_2)_3(tmen)_3][BPh_4]$·$[CoCl_2(tmen)]$ which was isolated as co-crystallite **2**. Its formation can be explained as a result of the ionization process (2).[16] Attempts to abstract the Cl^- ion from compounds **3** and

$$3[CoCl_2(tmen)] \rightleftharpoons [Co_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl_2)_3(tmen)_3]^+ + Cl^- \quad (2)$$

4 using $NaBPh_4$ salt failed, giving solutions from which no tractable products were isolated.

Experimental

All manipulations were carried out under a dry dinitrogen or argon atmosphere, following standard Schlenk techniques. All solvents were distilled from the appropriate drying agents under dinitrogen prior to use. The compounds $CoCl_2$, $MnCl_2$ and tmen were obtained from Aldrich Chemical Co. Infrared spectra were recorded on a Perkin-Elmer 180 instrument in Nujol mulls. Magnetic susceptibilities were measured by the Faraday method within the temperature range 78–295 K. Corrections for diamagnetism were made with Pascal's constants.[23]

Syntheses

Dichloro(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)cobalt(II) 1. A suspension of $CoCl_2$ (12.6 g, 20 mmol) in CH_2Cl_2 (80 cm^3) containing tmen (3 cm^3, 20 mmol) was stirred for 4 h. The resulting dark blue solution was filtered off and the filtrate concentrated to 15 cm^3 (oil). After 3 weeks dark blue needle-shaped crystals of complex **1** separated. Yield: 1.6 g (32%) (Found: Cl, 28.7; Co, 24.1. $C_6H_{16}Cl_2CoN_2$ requires Cl, 28.8; Co, 23.95%), $\mu_{eff} = 4.83\ \mu_B$. IR (Nujol, cm^{-1}): 319s, 350vs, 371w, 441w, 472w, 501w, 588w, 722w, 768m, 803s, 930w, 955s, 1005s, 1025s, 1040m, 1061w, 1200w, 1208w, 1225m, 1268m and 1295m.

Bis(μ_3-chloro)tris(μ-chloro)tris(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)tricobalt(II) tetraphenylborate–dichloro(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)cobalt(II) 2. To a solution of $[CoCl_2(tmen)]$ (1.48 g, 6 mmol) in thf–toluene (1 : 1; 80 cm^3) was added $NaBPh_4$ (0.68 g, 2 mmol). The mixture was stirred for 4 h and precipitated NaCl which was filtered off. The filtrate was concentrated to 40 cm^3 and left to crystallize at room temperature. After 3 d blue-violet needle-shaped crystals of complex **2** were collected, washed with toluene and dried *in vacuo*. Yield: 1.23 g (64.4%) (Found: Cl, 19.65; Co, 18.5. $C_{48}H_{84}BCl_7Co_4N_8$ requires Cl, 19.55; Co, 18.6%). IR (Nujol, cm^{-1}): 316s, 348vs, 370w, 441w, 470w, 498w, 586w, 610w, 706s, 720 (sh), 730vs, 765m, 798vs, 845w, 930w, 952vs, 1003s, 1040m, 1061w, 1100w, 1122w, 1170w and 1195w.

***catena*-Dichloro(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)-manganese(II) 3.** To a slurry of $MnCl_2$ (1.26 g, 10 mmol) in thf (80 cm^3) was added tmen (1.5 cm^3, 10 mmol). The reaction mixture was stirred for 1 h and filtered. The volume of the filtrate was reduced *in vacuo* to *ca.* 40 cm^3 and left to crystallize at 273 K. After 48 h colourless needle-shaped crystals were filtered off, washed with hexane (3 × 5 cm^3) and dried *in vacuo*. Yield 0.9g (35%) (Found: Cl, 29.35; Mn, 22.35. $C_6H_{16}Cl_2MnN_2$ requires Cl, 29.0; Mn, 22.8%). IR (Nujol, cm^{-1}): 209vs, 285m, 375m, 442s, 455m, 476s, 588s, 720m, 770s, 801vs, 936 (sh), 952vs, 1009vs, 1025vs, 1050s, 1101s, 1125s, 1165vs, 1175s, 1190m, 1242s and 1282vs.

Hexa-μ-chloro-1 : 2-κ^2*Cl*;2 : 3-κ^2*Cl*;3 : 4-κ^2*Cl*-dichloro-1-κ*Cl*, 4κ*Cl*-tetrakis(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)-1κ^2*N*, 2κ^2*N*,3κ^2*N*,4κ^2*N*-tetramanganese(II) 4. To a slurry of $MnCl_2$ (3.8 g, 30 mmol) in CH_2Cl_2 (60 cm^3) was added tmen (4.5 cm^3, 30 mmol). The colourless solution was stirred for 30 min at room temperature and then filtered. The volume was reduced *in vacuo* to 30 cm^3 and left to crystallize at 273 K. After 3 d the colourless, needle-shaped crystals were filtered off and washed with hexane (3 × 5 cm^3). Yield 3.2 g (44.2%) (Found: Cl, 29.35; Mn, 22.65. $C_{24}H_{64}Cl_8Mn_4N_8$ requires Cl, 29.3; Mn, 22.7%). IR (Nujol, cm^{-1}): 285m, 375m, 442s, 455m, 476s, 588s, 720m, 770s, 801vs, 936 (sh), 952vs, 1009vs, 1025vs, 1050s, 1101s, 1125s, 1165vs, 1175s, 1190m, 1242s and 1282vs.

Crystallography

Intensities were collected using a Kuma KM4 four-circle diffractometer in the ω–2θ mode (with crystals of dimensions 0.5 × 0.4 × 0.4 for **1**, 0.5 × 0.5 × 0.5 for **2**, 0.5 × 0.4 × 0.4 for **3** and 0.6 × 0.5 × 0.4 for **4**) and Mo-Kα radiation (λ = 0.710 69 Å). The samples were cut from larger crystals. For all crystals the intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay. 2908 ($4 < 2\theta < 46$), 6490 ($4 < 2\theta < 47$), 1563 ($4 < 2\theta < 56$) and 5760 ($4 < 2\theta < 56°$) reflections were measured for **1**, **2**, **3** and **4**, respectively, from which 1663, 2414, 1009 and 3422 reflections with $I > 3.0\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELXL 93.[24] The

Table 5 Crystal and structure refinement data for complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_6H_{16}Cl_2CoN_2$	$C_{48}H_{84}BCl_7Co_4N_8$	$C_6H_{16}Cl_2MnN_2$	$C_{24}H_{64}Cl_8Mn_4N_8$
M	246.038	1267.913	242.048	484.096
T/K	298(1)	300(1)	298(1)	298(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a/Å	7.687(2)	31.639(4)	7.062(1)	13.977(5)
b/Å	13.202(3)	10.114(3)	10.656(2)	11.568(3)
c/Å	11.579(3)	38.097(9)	14.432(3)	13.701(5)
β/°	105.84(2)	91.24(2)	91.63(2)	101.77(3)
U/Å^3	1130(1)	12 188(5)	1086(1)	2169(2)
Z	4	8	4	2
D_c/g cm^{-3}	1.446(1)	1.382(1)	1.481(1)	1.483(1)
D_m/g cm^{-3}	1.438	1.376	1.493	1.479
μ/mm^{-1}	1.94	1.41	1.66	1.66
F(000)	508	5280	500	1000
hkl Ranges	0–10, 0–17, −14 to 14	0–28, 0–9, −38 to 36	0–6, 0–11, −15 to 15	−18 to 20, 0–15, 0–17
Unique reflections	1570	2373	1009	3289
Goodness of fit on F^2	1.075	1.045	1.079	1.064
Final $R1$	0.0325	0.0340	0.0238	0.0333
$wR2$	0.0793	0.0880	0.0632	0.0863

$R1 = \Sigma(F_o - F_c)/\Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

number of parameters refined was 100 for **1**, 613 for **2**, 100 for **3** and 196 for **4**. Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 25; real and imaginary components of anomalous dispersion were included for all non-H atoms. The hydrogen atoms were placed in calculated positions with d(C–H) = 1.08 Å and introduced as fixed contributors in the final stage of refinement. Absorption corrections following the DIFABS[26] procedure were applied: minimum and maximum corrections 0.900 and 1.066 for **1**, 0.925 and 1.052 for **2**, 0.935 and 1.090 for **3** and 0.958 and 1.094 for **4**. Weighting schemes of the form $w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.78P]$, $1/[\sigma^2(F_o^2) + (0.0641P)^2 + 44.93P]$, $1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.48P]$ and $1/[\sigma^2(F_o^2) + (0.0390P)^2 + 3.00P]$ where $P = (F_o^2 + 2F_c^2)/3$ were applied for **1**, **2**, **3** and **4**, respectively (refinement was on F^2). In the last cycle of the refinements, the maximum values of the ratio Δ/σ were < 0.005 Å. The final difference map showed a general background within −0.41 and 0.44 for **1**, −0.35 and 0.18 for **2**, −0.19 and 0.17 for **3** and −0.33 and 0.27 e Å^{-3} for **4**. The crystal data are summarized in Table 5.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/154.

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