DALTON
FULL PAPER

Anomalous reactions of the diamine $Me_2NCH_2NMe_2$ with nickel(II) and cobalt(II)

Peter B. Hitchcock, Darren A. Handley, Ting Hui Lee and G. Jeffery Leigh

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ

Received 9th August 2002, Accepted 8th October 2002
First published as an Advance Article on the web 20th November 2002

The diamine $Me_2NCH_2NMe_2$ (tmmn) is capable of forming simple adducts with most metal(II) ions of the first transition series, but with nickel and cobalt a variety of additional products can be obtained from its reaction with the dihalides. The diamine may be monodentate or bidentate, it may (formally) lose a hydride to generate a cation, and each N–C bond may break, generating new products containing additional methyl groups or the ions $(Me_2NH_2)^+$ or $(Me_2N{=}CH_2)^+$.

We have recently described[1] the coordinating properties of the diamines $Me_2N(CH_2)_nNMe_2$ (n = 1, 2, or 3) with chlorides and bromides of metal(II) ions of the first transition series. Generally they behave as simple chelating donors. We had hoped that some new evidence for the formation of trinuclear species of the type $[\{M(diamine)\}_3(\mu\text{-}Cl)_3(\mu^3\text{-}Cl)_2]^+$ might be forthcoming. In fact, only the diamine with $n = 2$ (tmen) shows any facility to support such trinuclear ions, and the diamine for $n = 3$ has never given rise to one.[2] However, for $n = 1$, $Me_2NCH_2NMe_2$ (tmmn), we did succeed in isolating one trinuclear compound, and a peculiarity of this product has led us to discover a whole range of reactions of this diamine which, we believe, are without precedent. Our initial studies are described in this paper.

Results

The reaction of nickel(II) chloride with two molar equivalents of tmmn in thf at reflux for 3 days produced a purple suspension containing some unreacted nickel chloride. After filtration and cooling, a mixture of blue (**1**) and red (**2**) crystals was obtained, and these crystals were separated by hand.

The blue crystals (**1**) gave a mass spectrum with a highest peak corresponding to the ion $[Ni_3Cl_4(OMe)(tmmn)_3]^+$ although there seemed to be no reagent present that could act as a source of the methyl group, except possibly for tmmn. Nevertheless, this was the first evidence we have obtained of a species of the type $[(metal)_3(anion)_5(diamine)_3]^+$ with a diamine other than $Me_2NCH_2CH_2NMe_2$ (tmen). This was confirmed by the X-ray structure analysis (Fig. 1). This showed the presence of two separate trinuclear cations. One is ordered and contains apical methoxide and chloride, $[NiCl_4(OMe)(tmmn)_3]^+$. The other, $[Ni_3Cl_4(OH)(tmmn)_3]^+$, has chloride and hydroxide randomly disordered between the two apical positions together with a small amount of $[Ni_3Cl_5(tmmn)_3]^+$. Because of the disorder the geometry involving the apical oxygen in this cation should be treated with caution.

The origin of the hydroxide was presumably adventitious water. The sensitivity to traces of moisture of similar systems with cobalt,[3] nickel[3] and vanadium,[4] which also give rise to homologous trinuclear species containing similar apical hydroxy species, has been reported by us earlier.

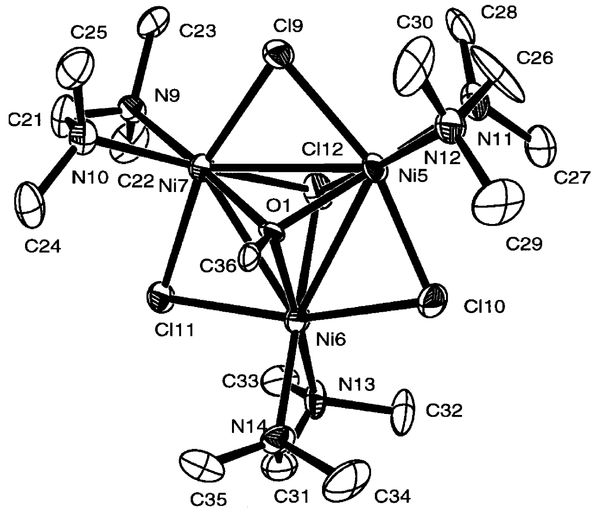


Fig. 1 The structure of the ordered cation $[Ni_3Cl_4(OMe)(tmmn)_3]^+$ in $[Ni_3Cl_4(OMe)(tmmn)_3][Ni_3Cl_4(OH)(tmmn)_3][NiCl_3(\eta^1\text{-}tmmn)]_2$.

Table 1 compares selected bond lengths in the $[Ni_3Cl_4(OH)(tmmn)_3]^+$, $[Ni_3Cl_4(OMe)(tmmn)_3]^+$ and $[Ni_3Cl_4(OH)(tmen)_3]^+$. It will be seen that the dimensions involving nickel and chlorides are very similar, and these, in turn are very similar to those seen in the other comparable tmen species.[3,4] The major differences concern the diamine, and even here they concern not so much the bond lengths as the bond angles N–Ni–N. These follow the pattern observed in comparable tmmn and tmen species.[5] Evidently the least energetically demanding deformation parameters in all these materials are the angles involving the nitrogen donor atoms, and not the bond lengths. This probably restricts the types of ligand that can form such trinuclear complexes.

The counter anion in the crystals of **1** is $[NiCl_3(tmmn)]^-$. The structure is shown in Fig. 2. The unexpected but not remarkable aspect of this structure is that the tmmn is monodentate. In our survey of structures of adducts of metal(II) halides with diamines, tmmn was always found to be bidentate,[1] with a rather small bite angle (*ca.* 65°) but with no unexpected metal stereochemistries. In this case the nickel is tetrahedral and four-coordinate, and one nitrogen donor of the tmmn is not coordinated. The Ni–Cl bond lengths are of the same order as those observed in the adducts $[NiCl_2(diamine)_2]$ (2.2–2.3 Å) and the Ni–N separation is also similar. One might assume that this means that bidentate tmmn is not particularly strained. The central carbon of the diamine contains an N–C–N angle of about 112°, not far from idealised tetrahedral.

DOI: 10.1039/b207818j

Table 1 Mean dimensions (Å, °) of cations $[Ni_3Cl_4(OH)(tmmn)_3]^+$ (this work), $[Ni_3Cl_4(OMe)(tmmn)_3]^+$ (this work) and $[Ni_3Cl_4(OH)(tmeda)_3]^+$ (ref. 3), in the solid state (173(2) K)

	$[Ni_3Cl_4(OH)(tmmn)_3]^{+\,a}$	$[Ni_3Cl_4(OMe)(tmmn)_3]^+$	$[Ni_3Cl_4(OH)(tmen)_3]^+$
$Ni–Cl_{equatorial}$	2.418(3)	2.417(3)	2.436(4)
$Ni–Cl_{capping}$	2.602(4)	2.513(4)	2.530(3)
$NiO_{capping}$	1.939(5)	2.035(4)	2.043(3)
Ni ··· Ni	2.998(4)	2.998(4)	3.026(3)
Ni–N	2.103(3)	2.115(3)	2.127(9)
$Cl_{eq}–Ni–Cl_{eq}$	163.27(7)	163.27(8)	163.2(1)
$Ni–Cl_{eq}–Ni$	76.65(7)	77.65(6)	76.6(1)
$Ni–Cl_{cap}–Ni$	70.37(9)	73.23(6)	73.57(11)
$NiO_{cap}–Ni$	101.31(9)	94.85(7)	95.8(4)
N–Ni–N	69.74(9)	67.21(9)	85.9(4)

[a] These dimensions may be affected by the disorder.

Table 2 Comparison of the dimensions (Å, °) of the anions $[NiCl_3(\eta^2\text{-tmmn})]^-$ (a) and $[NiCl_3(\eta^1\text{-tmmn})]^-$ (b)

Dimension (a)	Magnitude (a)	Dimension (b)	Magnitude (b)
Ni–Cl(1)	2.3020(9)	Ni(8)–C1–(13)	2.243(5)
Ni–Cl(2)	2. 3041(8)	Ni(8)–C1–(14)	2.260(4)
Ni–Cl(3)	2.3357(9)	Ni(8)–C1–(15)	2.244(4)
Ni–N(1)	2.147 (2)	Ni(8)–N(15)	2.040(11)
Ni–N(2)	2.123(2)		
N(1)–C(3)	1.475(3)	N(15)–C–(37)	1.420(15), 1.49(2)
N(2)–C(3)	1.479(3)	N(16)–C–(37)	1.397(17), 1.466(19)
Cl(1)–Ni–Cl(2)	97.64(3)	C1(13)–Ni(8)–CI(14)	109.41(17)
Cl(1)–Ni–Cl(3)	101.99(3)	C1(13)–Ni(8)–C1(15)	116.82(17)
Cl(2)–Ni–Cl(3)	105.98(3)	C1(14)–Ni(8)–Cl(15)	119.75(18)
N(1)–Ni–N(2)	66.96(7)		
N(1)–Ni–Cl(1)	155.62(6)	N(15)–Ni(8)–Cl(13)	102.6(4)
N(1)–Ni–Cl(2)	92.59(6)	N(15)–Ni(8)–C1(14)	101.9(3)
N(1)–Ni–Cl(3)	96.31(6)	N(15)–Ni(8)–C1(15)	103.3(3)
N(2)–Ni–Cl(1)	94.75(6)		
N(2)–Ni–Cl(2)	151.07(6)		
N(2)–Ni–Cl(3)	96.80(6)		
N(1)–C(3)–N(2)	105.77(17)	N(15)–C(37)–N(16)	111.8(11)
C(1)–N(1)–C(2)	108.44(19)	C(38)–N(15)–C(39)	109.5(13)
C(4)–N(2)–C(5)	109.3(2)	C(40)–N(16)–C(41)	110.0(10)

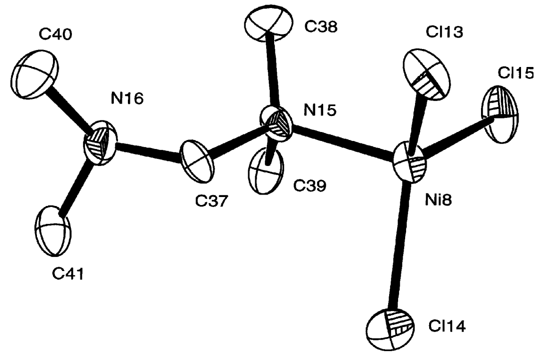


Fig. 2 The structure of the anion in $[Ni_3Cl_4(OMe)(tmmn)_3][Ni_3Cl_4(OH)(tmmn)_3][NiCl_3(\eta^1\text{-tmmn})]_2$.

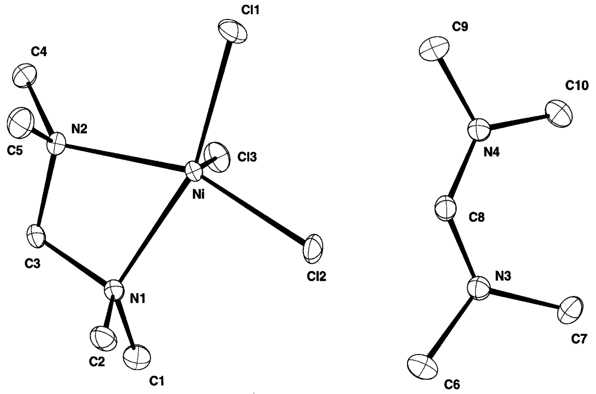


Fig. 3 The structures of the ions in $(Me_2NCHNMe_2)_2[NiCl_3(\eta^2\text{-tmmn})]$.

However, the structure of **2** challenges this assumption. The crystal (Fig. 3) contains an isomeric form of $[NiCl_3(tmmn)]^-$, in which the tmmn is bidentate. There are some possible hydrogen-bonding interactions that may be significant, but we do not feel that they are important. The angles about the central carbon of the tmmn in this complex is close to the ideal tetrahedral (see Table 2), and both the monodentate and bidentate tmmn have similar angles about a nitrogen coordinated to nickel, even though coordination about the nickel in this case is now distorted square pyramidal. The bite angle of the diamine, is 66.96(7)°, which is normal for bidentate tmmn, and the Ni–Cl bond lengths are *ca.* 2.3 Å. In the monodentate isomer they are marginally shorter, *ca.* 2.25 Å. This is not unexpected.

We do not know why this ion, $[NiCl_3(tmmn)]^-$, can exist in two isomeric forms. Although we have been unable to carry out structural studies in solution, it seems probable that there is little energy difference between the two forms, which, be it noted, crystallise from the same solution. There is precedent for the precise form of a molecule in the solid state to be imposed by the crystal, as presumed to be the case here. We have shown that $CoCl_2(tmen)$ may be monodentate or bidentate,[1,3] depending upon the crystal in which it finds itself. Another recent example appears to be $[Co_3(dpa)_4Cl_4]$ (dpa = $(C_5H_4N)_2N^-$) which can adopt a linear chain structure which may be either symmetrical or asymmetric, depending upon crystal form.[5]

Table 3 The dimensions (Å, °) of the cation in the structure of $(Me_2NCHNMe_2)[NiCl_3(\eta^2\text{-tmmn})]$

N(3)–C(7)	1.466(3)	N(3)–C(8)	1.307(3)
N(4)–C(8)	1.315(3)	N(4)–C(9)	1.466(3)
N(4)–C(10)	1.465(3)	N(3)–C(6)	1.465(3)
C(8)–N(3)–C(6)	118.5(2)	C(8)–N(3)–C(7)	126.9(2)
C(6)–N(3)–C(7)	114.6(2)	C(8)–N(4)–C(10)	126.2(2)
C(8)–N(4)–C(9)	118.7(2)	C(10)–N(4)–C(9)	115.0(2)
N(3)–C(8)–N(4)	129.5(2)		

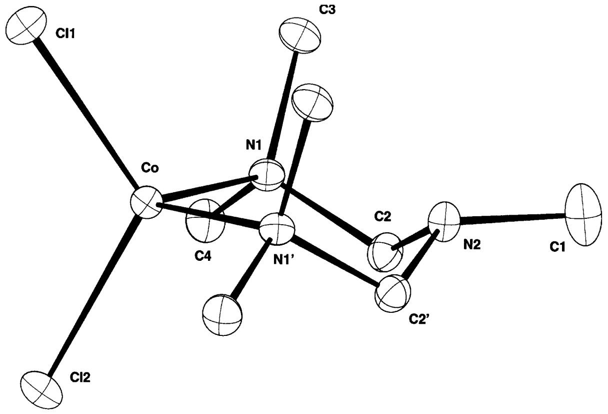


Fig. 4 The structure of $[CoCl_2(Me_2NCH_2NMeCH_2NMe_2)]$.

The counter anion in the crystal of **2** is a formamidium ion, $(Me_2NCHNMe_2)^+$. This is unexpected but not without precedent. The single hydrogen atom on the central carbon was located in a difference map and was refined. Several salts of this ion have been characterised. They are generally synthesised under acid conditions, though normally not from tmmn. However, it is well known that a methylene group bound between two amine nitrogen atoms can act as a formal hydride donor, and the metabolic role of tetrahydrofolic acid is a prime example.[6] The angles about the central carbon atom are suggestive of an sp^2 hybridisation, and the C–N bond lengths are shorter than would be expected for single bonds. The selected data in Table 3 are very similar to those observed in other salts containing this formamidium ion.

Thus with nickel(II) and tmmn we have observed an unusual isomerism but also some unexpected transformations. It is likely that tmmn can act as a source of methyl groups, and it is also clear that it can act as a formal hydride donor. Our experiments with cobalt(II) revealed ever more remarkable reactivity for tmmn.

The reaction of cobalt(II) chloride with tmmn in dichloromethane produces a blue suspension and oil. This very air-sensitive material is not, as we initially supposed, $[Co_3Cl_5(tmmn)_3]Cl$. Appropriate treatment with $Na[BPh_4]$ was not successful, but we eventually obtained crystals that were identified by X-ray structural analysis as $[CoCl_2(Me_2NCH_2NMeCH_2NMe_2)]$ (**4**) (Fig. 4 and Table 4). We have since developed a reproducible synthetic protocol for this material. The cobalt starting material in this case is the thf adduct of $CoCl_2$, which may be $CoCl_2{\cdot}thf$ or $CoCl_2{\cdot}thf_{1.5}$.[7] We choose to denote it by the former formula. The solvent is CH_2Cl_2.

In complex **4**, only the two end nitrogens are coordinated to the cobalt. The structure is remarkably similar to the complex of the diamine $Me_2NCH_2CH_2CH_2NMe_2$ (tmpd), with the exception that the central methylene is replaced by a NMe group.[1] The triamine is currently unrecorded in detail, though it is referred to in a patent[8] as a component of a mixture. Our attempts to synthesise it failed, probably because we tried to use acid conditions to catalyse the necessary formaldehyde/amine condensations. We were also unsuccessful in displacing it from the cobalt. More work is required in this area. However, the observation of its formation clearly implies that tmmn can undergo a series of bond-making and bond-breaking reactions, as indicated by our observations with nickel.

Table 4 Bond lengths (Å) and angles (°) for $[CoCl_2(Me_2NCH_2NMeCH_2NMe_2)]$

Co–N(1)	2.071(2)	Co–Cl(1)	2.243(1)
Co–Cl(2)	2.232(1)	N(1)–C(4)	1.484(3)
N(1)–C(3)	1.484(3)	N(1)–C(2)	1.488(3)
N(2)–C(2)	1.445(3)	N(2)–C(2)′	1.445(3)
N(2)–C(1)	1.457(5)		
N(1)′–Co–N(1)	101.64(10)	N(1)–Co–Cl(2)	108.09(6)
N(1)–Co–C1(1)	110.85(6)	Cl(2)–Co–C1(1)	116.27(4)
C(4)–N(1)–C(3)	108.84(19)	C(4)–N(1)–C(2)	108.35(18)
C(3)–N(1)–C(2)	109.82(19)	C(4)–N(1)–Co	110.56(15)
C(3)–N(1)–Co	110.73(15)	C(2)–N(1)–Co	108.50(14)
C(2)–N(2)–C(2)′	114.2(3)	C(2)–N(2)–C(1)	114.58(17)
N(2)–C(2)–N(1)	111.5(2)		

Symmetry operator: ′ *x*, ½ − *y*, *z*.

Table 5 Bond lengths (Å) and angles (°) for $(Me_2NH_2)(Me_2N{=}CH_2)[CoCl_4]$

Co–Cl(1)	2.2643(7)	N(1)–C(1)	1.479(3)
Co–Cl(3)	2.2675(7)	N(2)–C(5)	1.323(4)
Co–Cl(2)	2.2830(6)	N(2)–C(4)	1.407(4)
Co–Cl(4)	2.2849(6)	N(2)–C(3)	1.415(4)
N(l)–C(2)	1.471(3)		
Cl(1)–Co–Cl(3)	113.92(3)	Cl(2)–Co–Cl(4)	109.84(3)
C1(1)–Co–Cl(2)	107.96(3)	C(2)–N(1)–C(1)	113.3(2)
Cl(3)–Co–Cl(2)	108.95(3)	C(5)–N(2)–C(4)	120.8(3)
Cl(1)–Co–Cl(4)	109.73(3)	C(5)–N(2)–C(3)	122.2(3)
Cl(3)–Co–Cl(4)	106.41(3)	C(4)–N(2)–C(3)	116.8(3)

Repetition of the cobalt/tmmn reaction, but using thf rather than CH_2Cl_2 as a solvent, yields different products, the nature of which depends on the amount of thf present and also upon the conditions of crystallisation. All are salts containing the anion $[CoCl_4]^-$ and the cations in the preparative solution seem to consist of a mixture of $[Me_2NH_2]^+$ and $[Me_2N{=}CH_2]^+$. The salt isolated can apparently contain two cations of a single kind, or one of each, and which is obtained seems to depend very critically upon the conditions of crystallisation. The structures of $(Me_2NH_2)(Me_2N{=}CH_2)[CoCl_4]$ (**5**) (Fig. 5 and Table 5) and of $(Me_2NH_2)_2[CoCl_4]$ (**6**), (Table 6) which has already been reported,[9] were determined. Both crystallise in the same system, and the unit cells are of similar size. The structures are not exceptional, and, as usual, hydrogen bonding between the dimethylammonium ion and the anion is observed. In fact, both crystals contain the same structural element, with two $(Me_2NH_2)^+$ ions bridging between two $[CoCl_4]^-$ ions by a total of four separate hydrogen bonds (Fig. 6). The cation ($Me_2N{=}$

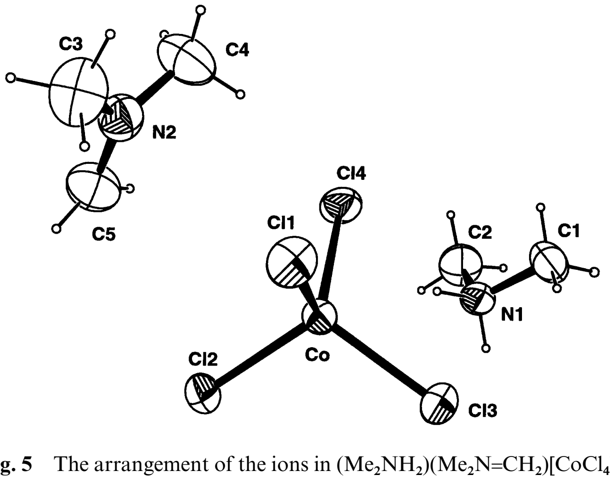


Fig. 5 The arrangement of the ions in $(Me_2NH_2)(Me_2N{=}CH_2)[CoCl_4]$.

Table 6 Bond lengths (Å) and angles (°) for $(Me_2NH_2)_2[CoCl_4]$

Co–Cl(1)	2.2766(13)	Co–Cl(3)	2.2888(11)
Co–Cl(2)	2.2664(11)	Co–Cl(4)	2.2597(13)
Cl(1)–Co–C1(2)	110.59(4)	Cl(2)–Co–Cl(3)	109.31(4)
Cl(1)–Co–Cl(3)	105.44(5)	Cl(2)–Co–Cl(4)	109.94(5)
Cl(1)–Co–Cl(4)	110.55(5)	CI(3)–Co–Cl(4)	110.94(5)

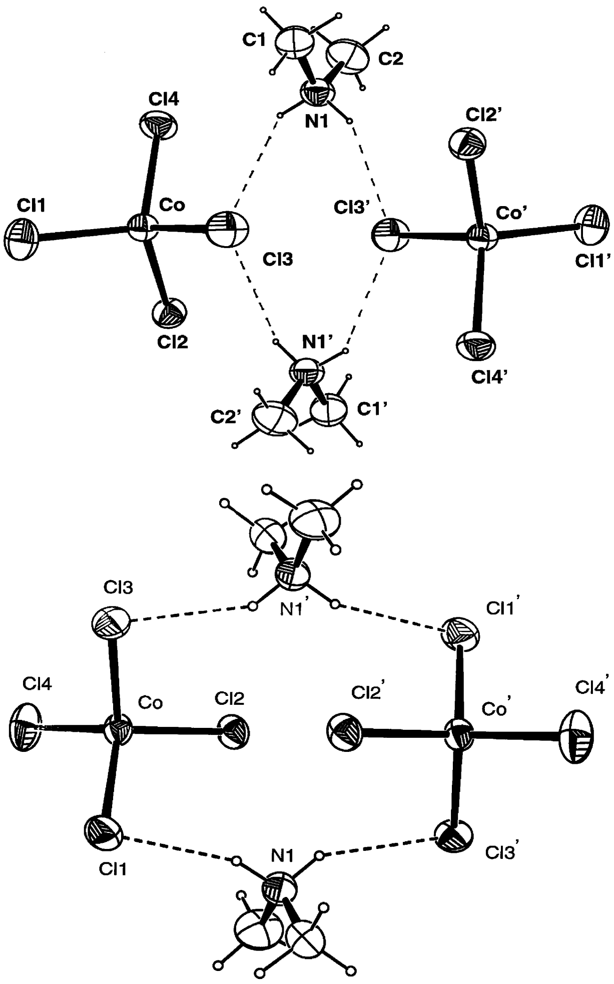


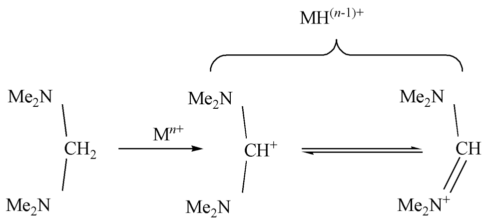
Fig. 6 The hydrogen-bonding chains in $(Me_2NH_2)(Me_2N{=}CH_2)[CoCl_4]$ (above) and in $(Me_2NH_2)_2[CoCl_4]$ (below).

$CH_2)^+$ is easily identifiable from the short N–C separation, and, when the admitted disorder in the structure is taken into consideration, its dimensions do not differ significantly for those reported in other structures containing this ion.[10]

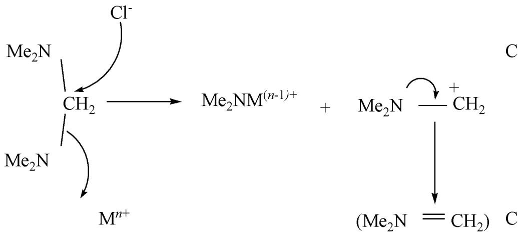
Another possible product from this system is $[\{CoCl_2(tmmn)\}_2]$, the preparation and structure of which we have described elsewhere[1] but which we quote below for comparison. This forms in CH_2Cl_2 if no trace of thf is present in the system.

During these researches, we also isolated an oil that seemed to be $(Me_2N{=}CH_2)(HCl_2)$. Its presence clearly hindered the isolation of crystalline compounds. However, our observations are all consistent with the break up of the tmmn, perhaps under the influence of the metal(II) Lewis acid and the thf.

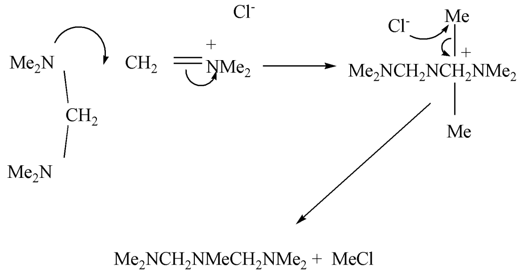
The reaction mechanism behind these transformations is not obvious, but clearly each N–C bond in tmmn is subject to cleavage. The reaction scheme accounts for all our products. The first series of reactions simply shows the loss of a proton from tmmn, as seems to be well understood, though in this case the acid present is a Lewis acid rather than a proton. The acid could, *a priori*, be a proton arising from adventitious water, but this seems unlikely because one might otherwise have expected to observe similar proton loss in our other related systems. We have no evidence yet for the formation of a metal hydride, let alone dihydrogen, though, as mentioned above, several salts containing $(Me_2NCHNMe_2)^+$ have been reported. The second sequence of reactions shows the breaking of an internal N–C bond. In this case we invoke the simultaneous action of the Lewis acid and of a halide base. We did not isolate any amido-complex, but salts containing both $(Me_2NH_2)^+$ and $(Me_2N{=}CH_2)^+$ have been characterised in our reactions. Finally, the reaction of this last cation, $(Me_2N{=}CH_2)^+$, with tmmn generates both the triamine, which we isolated as a complex, and methyl chloride. Again, we did not detect MeCl, nor did we look for it, but this kind of reaction could be the origin of the methyl group we detected in compound **1**. Clearly this scheme is speculative and it requires some confirmation in detail.



(1)



(2)



(3)

In an attempt to determine whether the $(Me_2N{=}CH_2)^+$ is itself a reactant in these systems, we mixed $NiBr_2$ and $(Me_2N{=}CH_2)Br$ in thf, and succeeded in isolating $[Me_2N{=}CH_2]_2[NiBr_4]$ as one product, which we characterised structurally. We shall report on these and related researches in a following paper.[11]

Experimental

All operations were carried out under an in inert atmosphere of dinitrogen using standard Schlenk techniques or under an inert atmosphere in an argon-filled glove box. Solvents were dried by standard procedures and distilled under dinitrogen prior to use. The commercial products $NiCl_2$ (99.99%, <100 ppm H_2O), $NiBr_2$ (99.99%, <100 ppm H_2O), $CoCl_2$ (99.99%, <100 ppm H_2O), and $Na[BPh_4]$ were used without further purification. *N*,*N*,*N*′,*N*′-Tetramethylmethanediamine (tmmn) was refluxed over molten sodium for 2 h and then distilled under dinitrogen prior to use. thf was refluxed over molten potassium and also distilled under dinitrogen prior to use. Microanalysis was by Ms Nicola Walker (Department of Chemistry, University of Surrey) using a Leenan CE 440 or Medac Ltd. elemental analyser. NMR spectra were obtained in an appropriate deuterated solvent using a Bruker 360 MHz instrument. Infrared spectra were obtained either as Nujol mulls spread on KBr plates or as KBr discs. Dr A. Abdul-Sada obtained the FAB and EI mass spectra using a Kratos M580RF and a VG Auto-

Table 7 Details of crystal-structure determination

	$[Ni_3Cl_4(OH)$-$(tmmn)_3][Ni_3Cl_4(OMe)$-$(tmmn)_3][NiCl_3(tmmn)]_2$ (**1**)	$(Me_2NCHNMe_2)$-$[NiCl_3(tmmn)]$ (**2**)	$[CoCl_2(pmdmt)]$ (**4**)	$(Me_2NH_2)(Me_2NCH_2)[CoCl_4]$ (**5**)	$(Me_2NH_2)_2[CoCl_4]$ (**6**)
Formula	$C_{41}H_{116}Cl_{14}N1_6Ni_8O_2$	$C_{10}H_{27}Cl_3N_4Ni$	$C_7H_{19}Cl_2CoN_3$	$C_5H_{16}Cl_{14}CoN_2$	$C_4H_{16}Cl_4CoN_2$
M_w/g mol^{-1}	1831.48	368.4	275.1	304.93	292.92
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*C*2 (no. 5)	$P2_1/n$	*Pnma* (no. 62)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	28.975(5)	15.257(3)	12.079(3)	8.8749(4)	8.4399(6)
b/Å	10.987(2)	7.922(2)	10.960(3)	10.0074(6)	11.3658(7)
c/Å	25.727(4)	15.488(5)	9.231(3)	15.0839(6)	13.4408(11)
β/°	102.266(14)	115.10(2)	90	95.553(3)	90.015(4)
V/Å^3	8003(2)	1695.2(8)	1222.1(6)	1333.4(1)	1289.32(16)
Z	4	4	4	4	4
Total reflections	7566	4216	5563	9316	7340
Unique reflections	7430 [*R*(int) = 0.067]	4077 [*R*(int) = 0.0325]	1547 [*R*(int) = 0.0533]	3869 [*R*(int = 0.042]	2130 [*R*(int = 0.041]
μ/cm^{-1}	2.35	1.61	1.81	2.05	2.12
Final *R*1 (all data)	0.0667	0.047	0.051	0.053	0.050
Final *wR*2 (all data)	0.1229	0.098	0.066	0.091	0.121

spec instrument, as appropriate. The ES mass spectra were obtained by Prof. Brian Nicholson (University of Waikato, New Zealand).

Crystallography

X-Ray crystal structure data were collected by the 2θ–ω scan method at 173(2) K using an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å). During processing, the data were corrected for absorption by semi-empirical ψ-scan methods. The structures were solved by direct methods in SHELXS and refined by full-matrix least-square methods in SHELXN.[12] All non-hydrogen atoms were refined anistropically. Details of the crystal-structure determinations are given in Table 7. Diagrams of the molecular structure of complexes were drawn with the ORTEP package.[13]

CCDC reference numbers 191669–191672 and 194217.

See http://www.rsc.org/suppdata/dt/b2/b207818j/ for crystallographic data in CIF or other electronic format.

Syntheses

$[Ni_3Cl_4(OH)(tmmn)_3][Ni_3Cl_4(OMe)(tmmn)_3][NiCl_3(tmmn)]_2$ (1). To a beige suspension of $NiCl_2$ (0.50 g, 6.2 mmol) in thf (30 cm^3), tmmn (1.5 cm^3, 11 mmol) was added. The reaction mixture was heated under reflux for 72 h. A yellow solid characterised as unreacted $NiCl_2$ was filtered from a purple solution. The filtrate was cooled to 0 °C and after a period of 2 weeks a mixture of large blue crystals (**1**) and smaller red crystals had separated from solution. The blue crystals were of sufficient size that they could be removed from solution using a spatula. Crystals of **1** decompose slowly when exposed to air. FAB-MS (*m*/*z*, rel. int.): 655 $\{Ni_3Cl_4(OMe)(tmmn)_3\}$ (14%), 553 $\{Ni_3Cl_4(OMe)(tmmn)_2\}$ (4%), 520 $\{Ni_3Cl_4(tmmn)_2\}$ (2%), 423 $\{Ni_2Cl_2(OMe)(tmmn)_2\}$ (24%), 211 {NiCl(OH)(tmmn)} (12%), 101 {tmmn} (41%).

$(Me_2NCHNMe_2)[NiCl_3(\eta^2\text{-tmmn})]$ (2). To a beige suspension of $NiCl_2$ (0.80 g, 6.2 mmol) in thf (60 cm^3), an excess of tmmn (3.0 cm^3, 23 mmol) was added. The reaction mixture was heated under reflux for 24 h. A blue–turquoise solid (**1**) was filtered from a cherry red solution. The turquoise solid turns green upon exposure to air. Yield 0.66 g (46%). A red crystalline solid (**2**) separated from the cherry red filtrate after it was cooled to −20 °C. The red crystals of **2** were isolated by filtration. They are very air-sensitive and turn green upon exposure to air. A small amount of the turquoise powder **1** was treated with thf (10 cm^3) and filtered to produce a red solution. This solution was layered with hexane (10 cm^3).

$[CoCl_2(pmdmt)]$ (4). An excess of tmmn (1.1 cm^3, 7.6 mmol) was added to a light blue suspension of $CoCl_2$·thf (1.1 g, 5.0 mmol) in CH_2Cl_2 (30 cm^3). The mixture was stirred for *ca.* 7 days and then concentrated to *ca.* 20 cm^3 *in vacuo*. Dark-blue crystals, suitable for X-ray structural analysis, were obtained upon layering with diethyl ether at room temperature. Yield: 0.4 g (29%).

$(H_2NMe_2)(Me_2N{=}CH_2)[CoCl_4]$ (5). To a light blue suspension of $CoCl_2$·thf (1.13 g, 5.6 mmol) in thf (30 cm^3) a large excess of tmmn (3.0 cm^3, 21 mmol) was added. The reaction mixture was stirred and a light blue oily solid was filtered from a purple–blue solution. The solid was dried under a stream dinitrogen for 2 h and then in *vacuo* for 4 h, but it still appeared oily. The solid was recrystallised from a thf solution layered with Et_2O to yield light blue crystals (**5**). The crystals were filtered from solution and dried under a stream of dinitrogen. Yield 0.26 g, (17%). Complex **5** is soluble in thf, ethanol and dichloromethane giving blue solutions. The analysis was higher in carbon than required but the structure of the selected crystals was unequivocal. Found: C, 23.1; H, 6.6; N, 10.5. $C_5H_{16}Cl_4CoN_2$ requires: C, 19.7; H, 5.3; N, 9.2%.

$(Me_2NH_2)_2[CoCl_4]$ (6). To a light blue suspension of $CoCl_2$·thf (1.0 g, 5.0 mmol) in thf (30 cm^3) a large excess of tmmn (3.0 cm^3, 21 mmol) was added. The reaction mixture was stirred for 4 days. A light blue solid was filtered from a purple–blue solution. Recrystallisation from a thf solution layered with Et_2O afforded light-blue crystals suitable for X-ray structural analysis. The purple–blue filtrate was layered with hexane to yield a dark-blue solid (0.6 g), which was recrystallised from thf layered with diethyl ether to yield more blue crystals. Found: C, 13.5; H, 5.7; N, 9.0. $C_4H_{16}Cl_4CoN_2$ requires: C, 16.4; H, 5.5; N, 9.6%.

$[\{CoCl_2(tmmn)_2\}_2]$. To a light blue suspension of $CoCl_2$ (0.60 g, 4.6 mmol) in dichloromethane (25 cm^3), a slight excess of tmmn (1.0 cm^3, 7.0 mmol) was added. The reaction was stirred for 5 h. A fine blue residue was filtered from the blue filtrate and was discarded. The blue–purple solution was reduced to *ca.* 10 cm^3 in vacuum and layered with Et_2O to produce dark blue crystals. Yield 0.78 g, 74%. Found: C, 24.8; H, 5.95; N, 11.6. $C_{10}H_{28}Cl_4Co_2N_4$ requires: C, 25.8; H, 6.05; N, 12.1%.

Acknowledgements

We acknowledge the award of an SERC Studentship to D. A. H.

References

1 D. A. Handley, P. B. Hitchcock, T.-H. Lee and G. J. Leigh, *Inorg. Chim. Acta*, 2001, **314**, 14.
2 D. J. Evans, P. B. Hitchcock, G. J. Leigh, B. K. Nicholson, A. C. Niedwieski, F. S. Nunes and J. S. Soares, *Inorg. Chim. Acta*, 2001, **319**, 147.
3 D. A. Handley, P. B. Hitchcock and G. J. Leigh, *Inorg. Chim. Acta*, 2001, **314**, 1.
4 P. B. Hitchcock, D. L. Hughes, L. F. Larkworthy, G. J. Leigh, C. J. Marmion, J. R. Sanders, G. W. Smith and J. S. de Souza, *J. Chem. Soc., Dalton Trans.*, 1997, 1127.
5 F. A. Cotton, C. A. Murillo and X.-P. Wang, *J. Chem. Soc., Dalton Trans.*, 1999, 3327; R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, K. Kirschbaum, C. A. Murillo, A. A. Pinkerton, A. J. Schultz and X.-P. Wang, *J. Am. Chem. Soc.*, 2000, **122**, 6226.
6 J. C. Fontecilla-Campus, C. E. Bugg, C. Temple, J. D. Rose, J. A. Montgomery and R. L. Kisliuk, *J. Am. Chem. Soc.*, 1979, **101**, 6114.
7 See, *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard and J. A. McCleverty, eds., Pergamon Press, Oxford, 1987, vol. 4, p. 828; for a more recent discussion see also: J.-C. Hierso, D. D. Ellis, A. L. Spek, E. Bouwman and J. Reedijk, *Chem. Commun.*, 2000, 1359.
8 I. Wiesner, L. Krudenc and V. Bruthans, *Czech Patent*, 131578, 1969; (*Chem. Abstr.*, 1970, **73**, 4517d).
9 A. H. Mahmoudkhani and V. Langer, *Acta Crystallogr., Sect. B*, 1999, **55**, 752.
10 G. R. Clark, G. L. Shaw, P. W. J. Shurman and M. J. Taylor, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3139.
11 P. B. Hitchcock, Ting Huei Lee and G. J. Leigh, in preparation.
12 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976; SHELXN, an extended version of SHELX-76, 1977; SHELXS, Program for Crystal Structure Determination, University of Göttingen, 1986; SHELX-93, Program for Crystal Structure Refinement, University of Göttingen, 1993.
13 ORTEP, Program for Diagrams, C. K. Johnson, ORNL Report 3794, Oak Ridge National Laboratory, Tennessee, revised 1991.