28. *Amine Compounds of the Transition Metals. Part III.* The Reaction of Some Transition-metal Chlorides with Anhydrous Ethylenediamine and Propylenediamine.*

By G. W. A. Fowles and W. R. McGregor.

The reaction of anhydrous ethylenediamine and propylenediamine with transition-metal chlorides has been studied. The more ionic chlorides, vanadium(III) chloride and chromium(III) chloride, are strongly solvated and form $[V\,en_3]Cl_3$, $[V\,pn_3]Cl_3$, and $[Cr\,en_3]Cl_3$ respectively, whereas the covalent titanium(IV), vanadium(IV), and molybdenum(V) chlorides are solvolysed by anhydrous ethylenediamine. Iron(III) chloride is first reduced to the iron(II) state and subsequently forms the "outer-orbital" complex $[Fe\,en_3]Cl_2$. The structure of the reaction products is discussed.

Whereas the ionic halides of metals of Groups IA, IIA, and IIIA react with ammonia to form simple ammoniates,[1] the ionic halides of the lower-valency states of the transition elements form the cobaltammine type of compound and the more covalent halides of these metals undergo ammonolysis with the formation of ammonobasic halides. While examining the analogous reactions of metal halides with amines, we have examined the reactions of transition-metal chlorides of both ionic and covalent type with anhydrous ethylenediamine and propylenediamine. These amines are interesting in that they can form especially stable chelate compounds with the transition metals.

Experimental

Materials.—Ethylenediamine (en) and propylenediamine (pn) were purified as described previously.[2] Vanadium(III) chloride was made by the thermal decomposition of vanadium(IV) chloride in an atmosphere of carbon dioxide.[3] Iron(III) chloride was prepared by direct chlorination of iron powder, and sublimed; reduction with hydrogen at 300° gave iron(II) chloride. Titanium(IV) chloride (from Messrs. British Drug Houses Ltd.) was refluxed with sodium amalgam and finally vacuum-distilled into sealed tubes. Anhydrous chromium(III) chloride was made by the action of carbonyl chloride on the heated hexahydrate.[4]

Analysis.—Chlorine, nitrogen, and vanadium were determined as previously described.[1] Iron and chromium were estimated by titration of their reduced solutions with potassium dichromate, and titanium by precipitation of the hydroxide followed by ignition to the oxide.

Reactions.—All reactions were carried out with anhydrous materials under rigorously anhydrous conditions, in the usual type of closed vacuum system.[1]

Reaction of vanadium(III) *chloride with ethylenediamine and propylenediamine.* Vanadium(III) chloride and excess of ethylenediamine were sealed in an ampoule; considerable heat was generated when reaction occurred, and after prolonged shaking a deep red-brown solution remained. On opening the ampoules and pumping away excess of amine (20 hr. at 100°) a homogeneous red-brown *solid* remained (Found: V, 14·9; Cl, 29·1; en, 54·1. $VCl_3,3en$ requires V, 15·1; Cl, 31·5; en, 53·4%). Because of the very viscous solution formed by the vanadium(III) chloride in ethylenediamine, the last traces of amine could only be removed by prolonged pumping; samples pumped for a shorter time contained more ethylenediamine.

The reaction of vanadium(III) chloride with propylenediamine gave a similar *product*; the analyses again show the high amine content which is found if the product is pumped for only a short time ($VCl_3,3pn$ requires V, 13·4; Cl, 28·0; pn, 58·6%).

The slightly low V : Cl ratio is attributed to a little thermal decomposition of vanadium(III) chloride when sealing off the storage tubes; and analysis of the chloride which had been thus sealed off gave a V : Cl ratio of 1 : 2·92.

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* Part II, Fowles and Pleass, *J.*, 1957, 2078.

[1] Fowles and Pleass, *J.*, 1957, 1674.
[2] Fowles, McGregor, and Symons, *J.*, 1957, 3329.
[3] Young and Smith, *Inorg. Synth.*, 1953, **4**, 128.
[4] Heisig, Fawkes, and Hedin, *Inorg. Synth.*, 1946, **2**, 193.

Time of pumping at 100°	V (%)	Cl (%)	pn (%)	Ratio V : Cl : pn
5 hr.	12·1	24·4	63·1	1 : 2·88 : 3·58
10 hr.	13·3	26·4	59·0	1 : 2·87 : 3·08
24 hr.	13·1	26·7	58·7	1 : 2·92 : 2·91

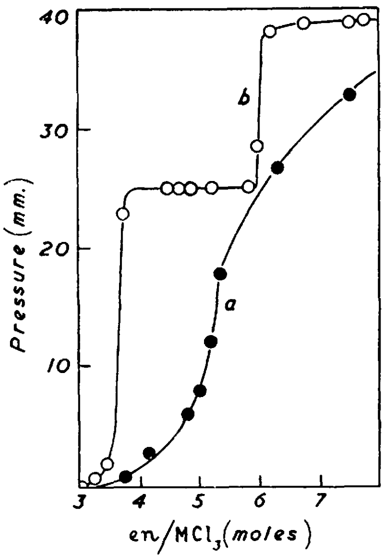
The analyses of these products indicate that vanadium(III) chloride reacts with anhydrous ethylenediamine and propylenediamine to give $VCl_3,3en$ and $VCl_3,3pn$ respectively, both of which are stable *in vacuo* up to 100°. While the difficulty of removing the last traces of amine could be accounted for by the viscous nature of the solutions formed by the compounds in the amine, it seemed possible that definite amounts of amine might be attached to the compounds in an " ammoniate " manner. A tensimetric investigation (Figure, *a*) of the vanadium(III) chloride–ethylenediamine system at 45° in a modified form of the Burg tensimeter [5] showed conclusively that only $VCl_3,3en$ was formed.

Reaction of chromium(III) *chloride with ethylenediamine*. Simple condensations of excess of ethylenediamine on a known weight of chromium(III) chloride in a weighed jointed tube, complete with stopcock, followed by removal of the excess of amine by prolonged pumping, showed that the chloride took up three molecules of ethylenediamine (Found: $CrCl_3$: en = 1 : 3·18, and 1 : 3·14). The violet chromium(III) chloride reacted with the ethylenediamine as it melted with the liberation of heat and the formation of a deep red solution. A yellow solid began to separate and after several hours a clear colourless supernatant liquid remained.

Ampoules of the reactants were made up, shaken, and opened, and the yellow solid washed with pure ethylenediamine. Evaporation of the filtrate left no residue, showing that no ethylenediamine hydrochloride was formed in the reaction. After overnight pumping at room temperature, the yellow *solid* was analysed (Found: Cr, 15·1; Cl, 29·7; en, 55·2%; Cr : Cl : en, 1·0 : 2·88 : 3·16; $CrCl_3,3en$ requires Cr, 15·4; Cl, 31·4; en, 53·2%). Its magnetic moment was 3·83 B.M., showing that chromium is still tervalent.

We conclude that chromium(III) chloride reacts with anhydrous ethylenediamine to give $CrCl_3,3en$.

Since the product is insoluble in ethylenediamine, there should be no difficulty in pumping off the amine, so that the high amine content of the product seems a definite indication of additional compound formation. This was confirmed by a tensimetric study at 45° (Figure, *b*) and 50°, which showed that $CrCl_3,3en$ takes up three additional molecules of ethylenediamine. From the dissociation pressures measured at 45° and 50°, ΔH for the equilibrium $CrCl_3,6en \rightleftharpoons CrCl_3,3en + 3en$ is 18·1 kcal./mole.



Tensimetric studies of the ethylenediamine–vanadium trichloride system ● *and the ethylenediamine–chromium trichloride system* ○ *at* 45°.

Reaction of iron(III) *chloride with ethylenediamine and propylenediamine*. Ethylenediamine reacted immediately with iron(III) chloride (in an ampoule) giving white fumes. After being shaken for several hours, a red-brown solution and an off-white solid remained; these were washed with fresh ethylenediamine until all traces of the red-brown colour of the associated solution had been removed. The red liquid contained almost no iron, but considerable amounts of chloride ion; evaporation of ethylenediamine from this solution left a highly viscous red liquid, which gave some yellowish-white sublimate when heated to 160° *in vacuo*.

The white solid remaining after the initial filtration was pumped for several hours at 45° (Found: Fe, 17·3; Cl, 21·3; en, 61·4%; Fe : Cl : en, 1 : 1·94 : 3·31. $FeCl_2,3en$ requires Fe, 18·2; Cl, 23·1; en, 58·7%). Its magnetic moment was 5·45 B.M.

The analysis and colour of the solid suggest that iron(III) chloride has been reduced to give an iron(II) compound, although the magnetic moment is considerably higher than a simple spin-only formula would predict (4·9 B.M.). As it seemed possible that this high value might arise from traces of iron in the iron(III) chloride, this was purified further by sublimation and

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[5] Sanderson, " Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 79.

reduced to iron(II) chloride; this reacted with ethylenediamine to give a colourless solution and a white solid (Found: Fe, 18·2; Cl, 23·0; en, 58·8%) which had a magnetic moment of 5·45 B.M. A direct titration of the white product of the iron(III) chloride–ethylenediamine reaction confirmed the bivalency of iron.

We may therefore conclude that iron(III) chloride is reduced by anhydrous ethylenediamine to give $FeCl_2$,3en. The red solution which is formed contains ethylenediamine hydrochloride, but no iron, and the red colour is evidently associated with the oxidation products of the amine.

Iron(III) chloride reacted more slowly, but otherwise similarly, with anhydrous propylenediamine.

Reaction of titanium(IV) *chloride with ethylenediamine.* The initial reaction gave an orange-red solid, which gradually became paler; an almost colourless solid and a clear supernatant liquid finally remained. On being washed with fresh ethylenediamine, followed by pumping, a colourless diamagnetic solid was obtained which had an analysis corresponding to $TiCl_{2.02}N_{3.91}$ (Found: Ti, 13·6; Cl, 20·4%). The filtrate contained large amounts of ethylenediamine hydrochloride.

In one experiment, the use of slightly moist ethylenediamine gave a multicoloured initial product which finally became dirty grey.

Reaction of vanadium(IV) *chloride and molybdenum*(V) *chloride with ethylenediamine.* Vanadium(IV) chloride reacts vigorously with ethylenediamine, initially forming white fumes, and subsequently a deep red-brown solution. Evaporation of ethylenediamine from the solution was very difficult because of its viscosity, and even after pumping for many hours at 70—100° the VCl_4 : en ratio was still 1 : 4·6.

Molybdenum(V) chloride also gave white fumes in its initial reaction with ethylenediamine, and finally formed a very dark brown solution with a little undissolved brown solid.

The products of these two reactions were evidently mixtures of ethylenediamine hydrochloride with some amino-basic chloride; but since these could not be separated (as could the product from titanium) by washing with ethylenediamine, the reactions were not studied in detail.

Magnetic Moments.—These were determined at room temperature on a Gouy balance.

DISCUSSION

Meyer and Backa [6] showed that vanadium(III) chloride forms a cobaltammine type of compound, $[V(NH_3)_6]Cl_3$, with ammonia. This is much less stable to air and moisture than the corresponding chromium compound formed from liquid ammonia and chromium(III) chloride; [7] this may be readily understood since the tervalent vanadium atom still has a vacant 3*d* orbital and should accordingly form labile octahedral complexes.[8]

We might expect both vanadium(III) chloride and chromium(III) chloride to form chelate compounds with diamines, in which both amino-groups co-ordinate with the metal. We expect the vanadium(III) compounds to be labile, so that they would be isolated only under rigorously anhydrous conditions. The reaction of vanadium(III) chloride with both anhydrous ethylenediamine and propylenediamine does give $[V\,en_3]Cl_3$ and $[V\,pn_3]Cl_3$ respectively, and although free diamine can only be removed from the compounds with difficulty, tensimetric studies prove that trisethylenediaminevanadium(III) chloride does not form a true compound with additional ethylenediamine.

We should expect chromium(III) chloride to form an inert compound with ethylenediamine: hydrated trisethylenediaminechromium(III) chloride is formed even from aqueous solutions of ethylenediamine.[9] The greater stability of this compound than of a hydrated chromium(III) ion may be attributed to the chelation associated with the ethylenediamine molecule. Pollinson and Bailar [7] and Linhard and Weigel [10] noted that a yellow compound is formed from anhydrous ethylenediamine and chromium(III) chloride,

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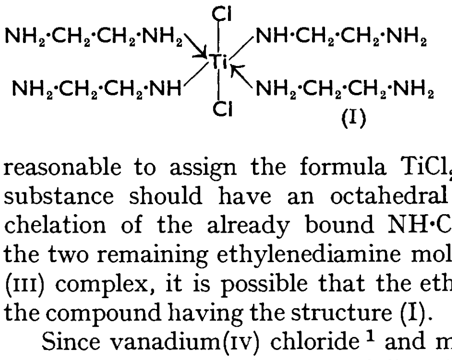
[6] Meyer and Backa, *Z. anorg. Chem.*, 1924, **135**, 177.
[7] Pollinson and Bailar, *J. Amer. Chem. Soc.*, 1943, **65**, 250.
[8] Taube, *Chem. Rev.*, 1952, **50**, 69.
[9] Balthis and Bailar, *J. Amer. Chem. Soc.*, 1936, **58**, 1474.
[10] Linhard and Weigel, *Z. anorg. Chem.*, 1953, **271**, 115.

but both pairs of authors dissolved this substance in water and precipitated the hydrated trisethylenediaminechromium(III) chloride. Our results show that the non-hydrated complex can be readily obtained under anhydrous conditions, but that it may take up three further molecules of ethylenediamine. These three extra ethylenediamine molecules are held quite weakly ($\Delta H = 18{\cdot}1$ kcal./mole) so that the substance $CrCl_3,6en$ is probably trisethylenediaminechromium(III) chloride with the three other ethylenediamine molecules bonded by ion–dipole forces, *i.e.*, $[Cr\ en_3]Cl_3,3en$. Alternatively, the substance $CrCl_3,6en$ may have a structure analogous to that of $[Cr(NH_3)_6]Cl_3$, with one amino-group of each ethylenediamine molecule bonded directly to the chromium atom; with the removal of a diamine molecule, the vacant co-ordination position on the chromium atom could be taken up by the other amino-group of a co-ordinated ethylenediamine molecule. The tensimetric investigation favours the first interpretation, since it does not indicate any intermediate steps in the process

$$CrCl_3,6en \longrightarrow CrCl_3,3en$$

The magnetic moment of 3·83 B.M. confirms the tervalent nature of chromium in the complex, although it cannot distinguish between the alternative orbitals which might be used for bonding—" inner," $3d^24s4p^3$, or " outer," $4s4p^34d^2$. Since the complex is inert, however, neither of the $3d$ orbitals can be vacant, so that the complex must be an inner-orbital one, with the chromium atom using its $3d^24s4p^3$ orbitals for bonding with the nitrogen atoms of the ethylenediamine molecules.

Investigations of the reaction of titanium(IV) chloride with ammonia,[11] and with methylamine and dimethylamine,[12] show that solvolysis occurs with the formation of ammono-basic and amino-basic titanium(IV) chlorides respectively. We should, therefore, expect titanium(IV) chloride to form some amino-basic chloride when it reacts with ethylenediamine, and an insoluble colourless substance $TiCl_2en_{3\cdot9}$ is indeed formed in the reaction; it may be easily separated from the ethylenediamine hydrochloride which is soluble in ethylenediamine. The diamagnetism of the product proves that titanium has not been reduced, while the analysis shows that two chlorine atoms have been replaced by ethylenediamine residues; it seems reasonable to assign the formula $TiCl_2(NH{\cdot}CH_2CH_2{\cdot}NH_2)_2,2en$ to the substance. This substance should have an octahedral configuration, with two positions taken up by chelation of the already bound $NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ unit through the amino-group, and the two remaining ethylenediamine molecules very weakly held. As with the chromium(III) complex, it is possible that the ethylenediamine molecules are only unidentate, with the compound having the structure (I).



(I)

Since vanadium(IV) chloride[1] and molybdenum(V) chloride[13] undergo solvolysis when they react with methylamine and dimethylamine, it is reasonable to attribute the formation of white fumes in their reaction with ethylenediamine to a similar cause, although separation and identification of the products was not possible.

Iron(III) chloride is reported to form an unstable hexammine with ammonia,[14] but with anhydrous ethylenediamine and propylenediamine any iron(III) compound which might form initially undergoes a subsequent reduction and the formation of $FeCl_2,3en$. This is evidently the same compound as that reported by Breuil[15] as the product of the iron(II) chloride–ethylenediamine reaction. $FeCl_2,3en$ is best considered as $[Fe\ en_3]Cl_2$, and the

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[11] Fowles and Pollard, *J.*, 1953, 2588.

[12] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

[13] Fowles and Sandy, unpublished observations.

[14] Newton-Friend, " Text-book of Inorganic Chemistry," Griffin & Co., Ltd., London, 1928, Vol. X, p. 127.

[15] Breuil, *Compt. rend.*, 1933, **196**, 2009.

magnetic moment of 5·45 B.M. shows that the complex is an "outer-orbital" one with the bivalent iron atom using $4s4p^3 4d^2$ orbitals for the bonding. The magnetic moment is appreciably greater than the "spin-only" formula would predict for four unpaired electrons (4·9 B.M.), but this is commonly found for outer-orbital iron(II) complexes, Klemm *et al.*[16] reporting a value of 5·3 B.M. for the analogous hexammine, $[Fe(NH_3)_6]Cl_2$, and may be attributed to incomplete quenching of the orbital contribution.

The mechanism of the reduction of iron(III) to iron(II) by the amine is not clear (cf. Part I for brief discussion of the reduction of halides by amines), and a discussion of the process is postponed.

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[16] Klemm, Jacobi, and Tilk, *Z. anorg. Chem.*, 1931, **201**, 1.