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Observations on the MCl_3–NMe_3 Systems (M = Ti, V and Cr): Isolation of the Mono-adducts $MCl_2 \cdot NMe_3$ (M = Ti and Cr) and $VCl_3 \cdot NMe_3$

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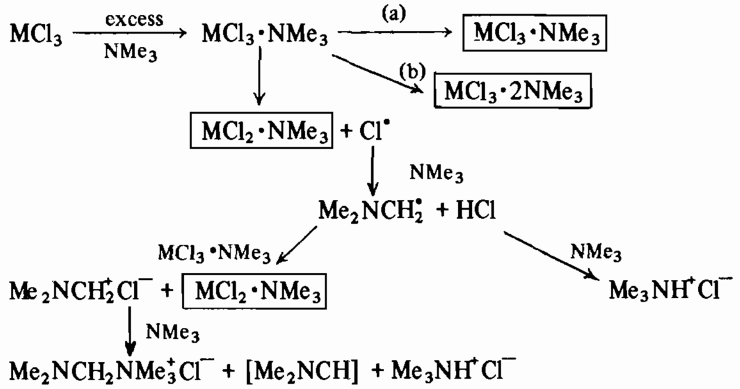
The five coordinate (D_{3h}) complexes $MX_3 \cdot 2NMe_3$ (M = Ti, V and Cr; X = Cl, Br) [1] are usually prepared by direct treatment of the appropriate anhydrous metal halide with an excess of trimethylamine. Fortuitously all are soluble in the parent amine, to give intense coloured solutions, and can be directly obtained by filtration and back-distillation within the double ampoule reaction vessel normally used. Recrystallisation from benzene solutions is not advised due to the accompanying decomposition [2] $2MCl_3 \cdot 2NMe_3 \rightarrow M_2Cl_6(NMe_3)_3 + NMe_3$. We now report other products of the MCl_3–NMe_3 system, namely the mono-adducts $MCl_2 \cdot MNe_3$ (M = Ti and Cr) and $VCl_3 \cdot NMe_3$, by following the reaction sequence to completion. In a typical reaction $CrCl_3$ (1.5 g) was sealed with dry NMe_3 (25 ml) in a double ampoule and careful filtration and evaporation of the characteristic purple-blue solution of $CrCl_3 \cdot 2NMe_3$ was continued *in situ* until the resulting extracted solution was colourless [3]. The residue was washed with dichloromethane, acetonitrile and benzene to remove amine oxidation product(s) and pumped *in vacuo* (T = 323 °K) for several hours to give the light grey product $CrCl_2 \cdot NMe_3$ (~0.1g). Calcd. C, 19.8; H, 5.0; N, 7.7; Cl, 39.0. Found. C, 19.8; H, 5.4; N, 7.3; Cl, 38.5. The titanium analogue was similarly obtained after removal of the bright blue $TiCl_3 \cdot 2NMe_3$ species. *Anal.* Calcd. for $C_3H_9NTiCl_2$: C, 20.2; H, 5.1; N, 7.9; Cl, 39.8. Found: C, 19.8; H, 5.3; N, 7.5; Cl, 39.0. In the vanadium case the chocolate brown $VCl_3 \cdot NMe_3$ remaining after extraction of the pink mauve $VCl_3 \cdot 2NMe_3$ constitued ~50% of the total product of the reaction. *Anal.* Calcd. for $C_3H_9NVCl_3$: C, 16.9; H, 4.2; N, 6.5; Cl, 49.1. Found: C, 16.5; H, 4.4; N, 6.7; Cl, 49.0. All are distinguished by their complete insolubility in a range of solvents. The ir spectra confirm the presence of coordinated NMe_3 and each shows a series of bands <400 cm^{-1} associated with $\nu(MCl)$ modes, *e.g.* $TiCl_2 \cdot NMe_3$ 394 vs, br, 353 s, br, 260 m, 185 s, br cm^{-1}; $VBr_3 \cdot NMe_3$ 386 s, br, 358 vs, 317 vs, br, 286 s, 204 s, br, 148 m cm^{-1}; $CrCl_2 \cdot NMe_3$ 392 vs, br, 340 s, br, 228 s, 192 s, br cm^{-1} consistent with a polymeric formulation.

Reduction of MCl_4 (M = Ti and V) by NMe_3 has been utilised as a preparative route to the corresponding tervalent species $MCl_3 \cdot 2NMe_3$ [4, 5]. M = Zr and Hf, where reduction is much less likely, simply give six coordinate $MCl_4 \cdot 2NMe_3$ complexes [6, 7]. For the VCl_4 reduction in particular Keisel and Schram [5] have identified $Me_2NCH_2^+Cl^-$ as main oxidation product which can further react via adduct formation and/or dehydrochloration with additional amine. A free radical mechanism involving Cl° elimination is favoured. A similar mechanism is proposed in the present instance, *viz.*,



Three possibilities, (a) immediate precipitation, (b) addition of a further ligand molecule to give soluble bis-adduct species, (c) elimination of Cl° from an initial mono-adduct lead to the observed products of the reactions. The M(II) species isolated comprised 1–2% of the total products; in neither case could $Me_2NCH_2^+Cl^-$ be positively identified. Extensive polymeric halogen bridging offers a reasonable stabilisation of the reduced $MCl_2 \cdot NMe_3$ species but these, as gauged by the relative amounts involved, are of secondary importance with respect to formation of $MCl_3 \cdot 2NMe_3$ following solvation. Specifically for vanadium the mono-adduct itself precipitates from solution presumably as a result of unfavourable lattice factors. Although there is no discernible redox it is conceivable that a very small amount of the reduced species $VCl_2 \cdot NMe_3$ is also incorporated. Interestingly the VBr_3–NMe_3 system similarly provides the bromo-analogue $VBr_3 \cdot NMe_3$ as an insoluble brown solid in addition to the expected $VBr_3 \cdot 2NMe_3$ soluble species [1b].

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References

1 a) See e.g. G. W. A. Fowles and P. T. Greene, *Chem. Comm.*, 784 (1966);
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c) P. T. Greene, B. J. Russ and J. S. Wood, *J. Chem. Soc. A*, 3636 (1971).
2 J. Hughes and G. R. Willey, *Inorg. Chim. Acta, 24,* L81 (1977).
3 The presence of a catalytic trace of zinc dust [1(b)] in the $CrCl_3$–NMe_3 system is unnecessary although reaction is thereby very slow, *e.g.* of two systems sealed at the same time the one with zinc dust included gave the characteristic blue-purple solution within 6 hrs whereas the one without took two weeks to achieve the same result. Both $TiCl_3$ and VCl_3 react directly with NMe_3 within several hours.
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