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Chromium(II)–Hydrazine Reactions: Polymeric $[Cr_2(O_2CCH_3)_4(\mu\text{-}N_2H_4)]_n$ and Cleavage of its Metal–Metal Bonds on Reaction with Carbon Dioxide Affording Mononuclear Chromium Carbazates

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The rapid reaction of anhydrous hydrazine with carbon dioxide to produce carbazic acid, which in the hydrazine solvent system will be present as $[N_2H_5][N_2H_3CO_2]$, can have detrimental consequences for the storage of the material as a rocket propellant in stainless steel systems [1]. The dissolved acid leaches metal ions from the steel surfaces into the bulk liquid where, as either solvated metal cations or metal carbazato-complexes, they may act as homogeneous catalysts for hydrazine decomposition. Recent investigations [2] have suggested that manganese and chromium may be particularly active metals in this respect so we have initiated a study aimed at identifying complexes of these metals capable of existence in hydrazine. Monopropellant specification hydrazine (maximum levels of H_2O and CO_2, 1% and 30 ppm, respectively) either alone, treated with additional carbon dioxide, or diluted by inert solvents, has been used in this work. We report here some of our findings on chromium complexes.

The only previously well-characterized [3] chromium(II)–hydrazine complexes are of the type $[CrX_2(\mu\text{-}N_2H_4)_2]_n$ (X = halide) and we have found several new routes to these compounds e.g. reactions between anhydrous chromium(II) chloride or $CrCl_2(NCMe)_2$ with methanol solutions of hydrazine.

We now report that $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ reacts with hydrazine in deoxygenated ethanol under nitrogen to give air-sensitive, orange $[Cr_2(O_2CCH_3)_4(\mu\text{-}N_2H_4)]_n$ (*Anal.* Calc. for $C_8H_{16}Cr_2N_2O_8$: C, 25.8; H, 4.3; N, 7.5. Found: C, 25.3; H, 4.3; N, 7.5%). The essential diamagnetism (χ_M^{corr}, 273 cm^3 mol^{-1}), diffuse reflectance spectrum (478, 360, 333 and 294 nm) and infrared spectrum [4] support a structure in which the quadruple metal–metal bond of the hydrate is retained but axial bridging hydrazine replaces the water generating a chain polymer with alternating dichromium(II) and hydrazine units as in $[Cr_2(O_2CCH_3)_4(\mu\text{-pyrazine})]_n$ [5].

When this complex is treated under nitrogen with carbazic acid, preformed from aqueous hydrazine and carbon dioxide, a more air-stable, lilac solid, insoluble in all common solvents is rapidly produced. This product, isolated as a monohydrate, has been identified as the new carbazato-complex $[Cr(O_2CNHNH_2)_2(H_2O)]_n$ (*Anal.* Calc. for $C_2H_8CrN_4O_5$: C, 10.9; H, 3.7; N, 25.5; Cr, 23.6. Found: C, 11.2; H, 3.1; N, 25.9; Cr, 23.3%.). The infrared spectrum indicates [4] the presence of *O,N*-chelating carbazate ligands, although additional metal–carbazate oxygen bridging interactions are likely to be present producing an octahedral layer structure as in $[Cd(O_2CNHNH_2)_2]_n \cdot nH_2O$ [6]. Confirmation of the presence of mononuclear high-spin chromium(II) rests with the magnetic moment (4.73 μ_B at 298 K), the diffuse reflectance visible spectrum (broad band with a maximum at 550 nm; $^5E_g \rightarrow {}^5T_{2g}$ in O_h symmetry), decomposition in concentrated hydrochloric acid under nitrogen generating $[Cr(H_2O)_6]^{2+}$, and a redox titrimetric determination.*

Although TGA and DTA evidence (exothermic peak at 214 °C under argon) indicates that on heating the water of $[Cr(O_2CNHNH_2)_2(H_2O)]_n$ is lost prior to complete decomposition of the carbazate groups (further exothermic peak at 304 °C), it could not be removed using dehydrating agents such as 2,2-dimethoxypropane [7] nor could it be replaced by other donor molecules.

In summary, (Scheme 1), the initial product of the reaction between $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ and hydrazine is $[Cr_2(O_2CCH_3)_4(\mu\text{-}N_2H_4)]_n$, the quadruple metal–metal bond of which is cleaved on reaction with carbon dioxide and additional hydrazine yielding mononuclear $[Cr(O_2CNHNH_2)_2(H_2O)]_n$, bridging hydrazine and acetate ligands being replaced by carbazate anions.

The complex $[Cr(O_2CNHNH_2)_2(H_2O)]_n$ can also be prepared under nitrogen by several other routes, e.g. (i) direct reaction of $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ with hydrazine and carbon dioxide in refluxing methanol, (ii) reactions of $CrCl_2 \cdot 4H_2O$ or $CrBr_2 \cdot 6H_2O$ with either aqueous hydrazine and carbon dioxide or preformed carbazic acid and (iii) reactions of $[CrX_2(\mu\text{-}N_2H_4)_2]_n$ (X = Cl or Br) with hydrazine and carbon dioxide.

When insoluble $[Cr(O_2CNHNH_2)_2(H_2O)]_n$ is treated with additional aqueous hydrazine and carbon dioxide gas is passed into the mixture, a further

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*Decomposition of a sample under basic conditions liberates N_2H_4 and Cr(II) both of which reduce added excess $[Fe(CN)_6]^{3-}$ generating 9 mol of $[Fe(CN)_6]^{4-}$ per mol of complex. This result is only compatible with the presence of Cr(II) and 2 hydrazino-groups *i.e.* $1Cr(II) \equiv 1[Fe(CN)_6]^{4-}$ and $2N_2H_4 \equiv 8[Fe(CN)_6]^{4-}$.

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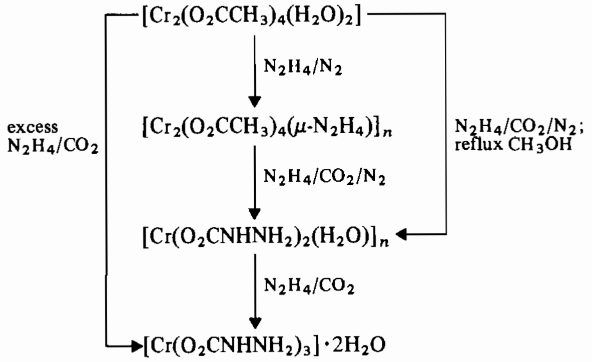

Scheme 1. Chromium–hydrazine and –carbazate complexes.

slow reaction ensues. A bright red colour develops in the solution from which air-stable chromium(III) carbazate $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ [1, 8] can subsequently be isolated. As judged by electronic spectral evidence* and the isolation of solid products, the same chromium(III) compound is slowly formed when any one of a range of chromium(II) complexes, e.g. hydrated halides, $[CrCl_2(\mu\text{-}N_2H_4)_2]_n$ or $[Cr_2(O_2CCH_3)_4(H_2O)_2]$, are treated with excess aqueous hydrazine and carbon dioxide. This reaction proceeds both in the presence and absence of air, suggesting that hydrazine or hydrazinium cations may be involved in the oxidation. Although hydrazine usually behaves as a ligand with reducing capability, thermodynamic considerations show that it can behave as an oxidising agent being itself reduced to ammonia. Indeed, we have observed [9] that anhydrous hydrazine reacts with anhydrous chromium(II) chloride to produce a chromium(III) species and from a study [10] of the kinetics of the reaction between chromium(II) and hydrazine in perchlorate media it has been proposed that the products are chromium(III) and ammonia.

The insolubility of both $[Cr(O_2CNHNH_2)_2(H_2O)]_n$ and $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ in a wide variety of solvents, including water, and the lack of success in replacing water in these compounds by other ligands suggests that intermolecular forces are unusually strong, presumably through a complex network of hydrogen-bonds involving the carbazate NH, NH_2 and CO_2-groups and the water molecules in the manner found in the related glycinato-complex $[Cr(O_2CCH_2NH_2)_3]\cdot H_2O$ [11].

This lack of solubility has frustrated attempts to produce crystals suitable for X-ray crystallographic studies of the nature of the hydrogen-bonding.

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*Diffuse reflectance spectrum of solid $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$: 698(vw), 523(s), 395(m) nm; N_2H_4solution: 700 (1.7), 522 (48), 402 (53) nm (ϵ in parentheses). $^4A_{2g} \rightarrow {}^2E_g$, $\rightarrow {}^4T_{2g}$ and $\rightarrow {}^4T_{1g}$, respectively in O_h symmetry.