Isolation of Trioxodinitrato(II) Complexes of Some First Row Transition Metal Ions

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Summary High-spin, heat- and light-sensitive tris[trioxodinitrato(II)] complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} have been isolated using the $[Co(NH_3)_6]^{3+}$ ion as a large counterion.

THE existence in aqueous solution of trioxodinitrato(II) complexes of Ni^{2+} and Pb^{2+} has been reported in which the trioxodinitrate(II) ion ($N_2O_3^{2-}$) functions as a bidentate ligand probably co-ordinating through the *cis*-oxygen atoms.[1] The distance between the *cis*-oxygen atoms (2·52 Å) found in $Na_2N_2O_3\cdot H_2O$[2] strongly supports formulation of the $N_2O_3^{2-}$ ion as a bidentate ligand. We report the first isolation of crystalline trioxodinitrato(II) complexes using the $[Co(NH_3)_6]^{3+}$ ion as a large counterion to stabilize the complex ion in the solid state.

Tris[trioxodinitrato(II)] complexes with the general formula $[Co(NH_3)_6]_4[M^{II}(N_2O_3)_3]_3\cdot 3H_2O$ where M^{II} = Mn, Fe, Co, or Ni are formed in aqueous solution under a nitrogen atmosphere from $Na_2N_2O_3$[3], $[Co(NH_3)_6]Cl_3$ and the appropriate transition metal chloride [equation (1)]. In a typical preparation a solution containing a 3 : 1 molar ratio of $Na_2N_2O_3$ and $CoCl_2\cdot 6H_2O$ is added slowly to a solution containing an excess of $[Co(NH_3)_6]Cl_3$. Crystallization of the complexes occurs rapidly with Mn^{2+}, Fe^{2+}, and Co^{2+}, but slowly with Ni^{2+}. The Fe^{3+} complex $[Co(NH_3)_6][Fe(N_2O_3)_3]\cdot 3H_2O$ was prepared by oxidation with O_2 gas of a solution containing a 5 : 1 molar ratio of $Na_2N_2O_3$ and $FeCl_2\cdot 6H_2O$ followed by addition of an excess of $[Co(NH_3)_6]Cl_3$. An intense charge-transfer band at 23,800 cm^{-1} appears upon oxidation to the Fe^{3+} complex.

$$4[Co(NH_3)_6]Cl_3 + 3\,MCl_2\cdot 6H_2O + 9\,Na_2N_2O_3 \xrightarrow[H_2O]{0\,^{\circ}C} [Co(NH_3)_6]_4[M^{II}(N_2O_3)_3]_3\cdot 3H_2O + 15\,H_2O \qquad M^{II} = \text{Mn, Fe, Co, or Ni} \qquad (1)$$

All complexes showed strong i.r. bands in the regions 1395—1370, 1260—1240, 1080—1050, and 960—940 cm^{-1} characteristic of the N=N and N–O stretching frequencies of the trioxodinitrate(II) ion[4] in addition to i.r. bands characteristic of the $[Co(NH_3)_6]^{3+}$ ion.[5] The deuteriated complexes $[Co(ND_3)_6]_4[M^{II}(N_2O_3)_3]_3\cdot 3D_2O$ where M^{II} = Co, Mn, or Ni were prepared to confirm the i.r. assignments. The stretching frequencies found in the complexes differ only slightly from those found in $Na_2N_2O_3$ and other simple salts containing the $N_2O_3^{2-}$ ion.

$[Co(NH_3)_6]_4[Co(N_2O_3)_3]_3\cdot 3H_2O$ slowly rearranges upon stirring in air-free water to form a new complex $[Co(NH_3)_6]_2[Co_2(N_2O_3)_5]$ [equation (2)]. $[Co(NH_3)_6]_2[Co_2(N_2O_3)_5]$ can also be prepared directly in aqueous solution from a 2·5 : 1 : 1 molar ratio of $Na_2N_2O_3$, $CoCl_2\cdot 6H_2O$, and $[Co(NH_3)_6]Cl_3$. The complexity of the i.r. spectrum of $[Co(NH_3)_6]_2[Co_2(N_2O_3)_5]$ in comparison to that of $[Co(NH_3)_6]_4[Co(N_2O_3)_3]_3\cdot 3H_2O$ may indicate the presence of a bridging trioxodinitrate(II) ligand in the $[Co_2(N_2O_3)_5]^{6-}$ anion.

$$2[Co(NH_3)_6]_4[Co(N_2O_3)_3]_3\cdot 3H_2O \xrightarrow{\text{air-free } H_2O} 3[Co(NH_3)_6]_2[Co_2(N_2O_3)_5] + 2[Co(NH_3)_6]^{3+} + 3N_2O_3^{2-} + 12\,H_2O \qquad (2)$$

The reported complexes are all thermally and photochemically unstable decomposing with evolution of NH_3 and NO upon exposure to sunlight for a few hours or upon heating *in vacuo* above 50 °C. The decomposed complexes show strong i.r. bands in the region 1880—1700 cm^{-1} characteristic of co-ordinated NO. Attempts at isolating nitrosyl complexes from the thermally decomposed complexes have not yielded analytically pure materials.

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