

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

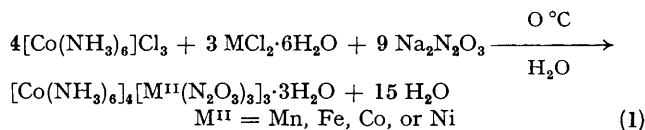
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Summary High-spin, heat- and light-sensitive tris[trioxodinitrato(II)] complexes of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Fe^{3+} have been isolated using the $[Co(NH_3)_6]^{3+}$ ion as a large counterion.

THE existence in aqueous solution of trioxodinitrato(II) complexes of Ni^{2+} and Pb^{2+} has been reported in which the trioxodinitrato(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.

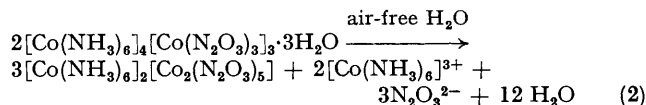
Tris[trioxodinitrato(II)] complexes with the general formula $[Co(NH_3)_6]_4[M^{II}(N_2O_3)_3]_3 \cdot 3H_2O$ where $M^{II} = Mn, Fe, Co,$ or Ni are formed in aqueous solution under a nitrogen atmosphere from $Na_2N_2O_3$, $[Co(NH_3)_6]Cl_3$ and the appropriate transition metal chloride [equation (1)]. 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 $23,800\text{ cm}^{-1}$ appears upon oxidation to the Fe^{3+} complex.

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 trioxodinitrato(II) ion⁴ 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 trioxodinitrato(II) ligand in the $[Co_2(N_2O_3)_5]^{6-}$ anion.

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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