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Nickel(II) Tetrachloroaluminate[1]

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We have prepared the compound $Ni(AlCl_4)_2$ by direct reaction between $NiCl_2$ and Al_2Cl_6 at temperatures near 200° in a sealed silica tube. We found that the binary system $NiCl_2$–Al_2Cl_6 has an invariant phase equilibrium at a temperature in the range 205–215° among the four phases gas, liquid, and solid $Ni(AlCl_4)_2$ and a second nickel-containing phase that may be $NiCl_2$. Below this invariant point the stable solid phase is $Ni(AlCl_4)_2$ while above it the other solid phase is stable. These phase relations explain why Munday and Corbett[2] did not observe $Ni(AlCl_4)_2$ in this system; they worked at temperatures above the conversion point.

The $Ni(AlCl_4)_2$ was prepared by placing $NiCl_2$[3] and an excess of $AlCl_3$[4] in thick-walled silica tubes which were then evacuated and sealed. These tubes were heated in windowed furnaces and gently agitated in such a way as to maintain the liquid, solid, and gas phases in mutual contact.

When Al_2Cl_6 and vacuum-sublimed $NiCl_2$ were heated to 200°, the reaction to form $Ni(AlCl_4)_2$ proceeded very slowly. However, if the mixture was first heated to 250–270° for an extended period, then upon cooling to 200° the reaction to form $Ni(AlCl_4)_2$ proceeded at a much faster rate. The two solid phases were easily distinguished in these reactions by their different crystal habits and colors.

In the presence of excess Al_2Cl_6, $Ni(AlCl_4)_2$ may be recrystallized in a thermal gradient at temperatures near 200°. During this recrystallization it appears as though nickel(II) transport may take place in the gas phase.

$Ni(AlCl_4)_2$ was isolated by slowly evaporating excess Al_2Cl_6 in a thermal gradient. A 0.092-g sample was analyzed. *Anal.* Calcd for $Ni(AlCl_4)$: Ni, 14.81; Al, 13.62; Cl, 71.57. Found: Ni, 14.1; Al, 13.6; Cl, 71.57.

$Ni(AlCl_4)_2$ formed at 200° consists of reddish orange needles which single-crystal X-ray diffraction data show to be monoclinic with lattice parameters $a_0 = 12.72 \pm 0.01$ Å, $b_0 = 7.672 \pm 0.007$ Å, $c_0 = 11.47 \pm 0.02$ Å, and $\beta = 92° \, 10' \pm 5'$. Placement of four formula weights of $Ni(AlCl_4)_2$ in this unit cell leads to a predicted density of 2.353 ± 0.008 g/cm^3. The intensity distribution has systematic absences due to body centering of the lattice and a *c*-glide plane normal to *b;* the space group is therefore Ic or I2/c. The lattice dimensions, possible space groups, and individual reflection intensities indicate that $Ni(AlCl_4)_2$ is isostructural with $Co(AlCl_4)_2$,[5] in which MCl_6 octahedra share corners with $AlCl_4$ tetrahedra to form infinite chains along the *c* axis.

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[3] Prepared by the method of D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

[4] Prepared by the method of N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

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On the Preparation and Properties of the Complex Hydrazopentaamminecobalt(III) Perchlorate

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It is known that ammino–azido complexes undergo acid hydrolysis through an acid-promoted path.[1-3] The influence of H^+ concentration on the aquation rate and on the spectra[4] of these compounds has been explained by a reversible protonation of the coordinated azide group. However, the existence of such protonated species has not been proved directly nor have the compounds been isolated as solids. [The single example of an isolable protonated amminecobalt(III) complex reported so far is *cis*-$[Co(NH_3)_4(NO_2)(NO_2H)](NO_3)_2$, which may be obtained from a nitric acid solution of the conjugate base.[5] Nitro complexes are known to hydrolyze in acid solution through an acid-catalyzed path for which a protonated intermediate of the above type has been postulated.]

Here, we wish to report the preparation of and a preliminary study of the properties of the complex $[Co(NH_3)_5NHN_2](ClO_4)_3$.

During an investigation of the photochemical behavior of solid $[Co(NH_3)_5N_3](ClO_4)_2$ it was observed that the addition of 70% $HClO_4$ to a cold solution of azidopentaamminecobalt(III) perchlorate resulted in the precipitation of a product whose properties were different from those of the starting complex.

The electronic spectrum of its aqueous solution was similar to that of $[Co(NH_3)_5N_3](ClO_4)_2$ but a titration with standard NaOH showed that it behaves, in water solution, as a strong acid with an equivalent weight between 520 and 550. The presence of a H_3O^+ group in the solid was excluded since a check for water (Karl Fischer method) on a pyridine solution of the acidic product proved negative.

Calculations based on the equivalent weight of a typical sample (535) led to the empirical formula $[Co(NH_3)_5N_3](ClO_4)_2 \cdot 0.89HClO_4$, which was also consistent with the elemental analysis. *Anal.* Calcd for

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[4] G. C. Lalor, *ibid.*, *A*, 1 (1966).

[5] R. Ugo and R. D. Gillard, *ibid.*, *A*, 2078 (1967).