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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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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] T. C. F. Munday and J. D. Corbett, *Inorg. Chem.*, **5**, 1263 (1966).

[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).

[5] J. A Ibers, *Acta Cryst.*, **15**, 967 (1962).

Contribution from the Chemistry Department
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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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[1] G. C. Lalor and A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963).

[2] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

[3] P. J. Staples, *J. Chem. Soc., A*, 2731 (1968).

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

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

$[Co(NH_3)_5N_3](ClO_4)_2 \cdot 0.89HClO_4$: H, 3.36; N, 23.8. Calcd for $[Co(NH_3)_5N_3](ClO_4)_2$: H, 3.9; N, 29.1. Found: H, 3.2; N, 23.06.

However, the differences observed in both ir and reflectance spectra of the azide complex and the acidic product (*cf.* Figure 1A and B) suggest for the latter a specific interaction between the azide group and the proton. Azido–metal complexes show a strong ir absorption band around 2050 cm^{-1} due to the antisymmetric stretching mode of the N_3 group[6] while the corresponding symmetric vibration occurs at lower frequencies (1400–1200 cm^{-1}). [The antisymmetric vibration in azidopentaamminecobalt(III) *perchlorate* appears as a doublet (see Figure 1A) at 2075 and 2045 cm^{-1}. This splitting does not occur when ClO_4^- is replaced by other anions (Cl^- for instance) but is observed in other solid azidoamminecobalt(III) complexes.[7] An explanation for this fact may be given in terms of a crystallinity effect. Indeed, the ir spectrum of the complex in a D_2O solution shows only a single sharp absorption at 2045 cm^{-1}, in agreement with such interpretation.]

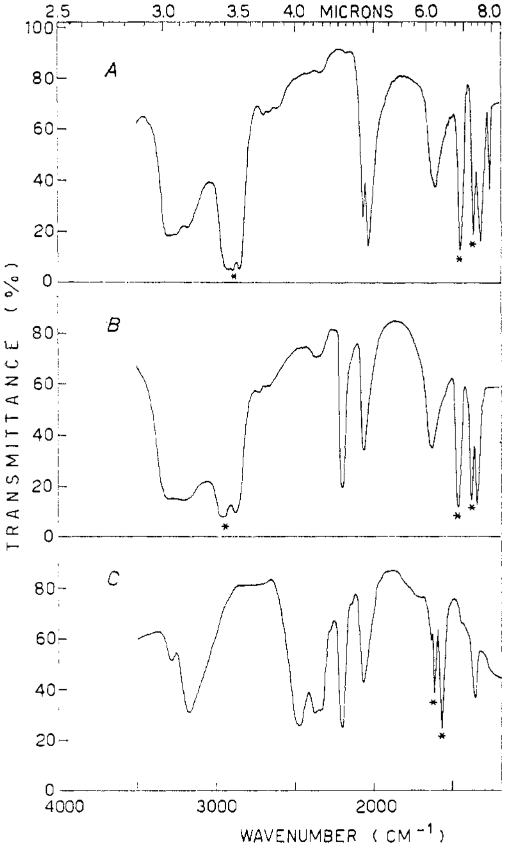
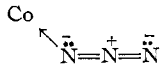


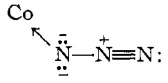
Figure 1.—Ir spectra of (A) $[Co(NH_3)_5N_3](ClO_4)_2$ (Nujol), (B) $[Co(NH_3)_5NHN_2](ClO_4)_3$ (Nujol), and (C) $[Co(ND_3)_5NHN_2](ClO_4)_3$ (hexachlorobutadiene). Starred bands are due to the mulling agents.

As shown in Figure 1B the antisymmetric stretching frequency of the N_3 group in the acidic product is blue-shifted by 150 cm^{-1} (2200 cm^{-1}) while the symmetric mode is no longer observed.

These effects strongly indicate the protonation of the azide group supported also by the appearance of an additional N–H stretching band. Such a band cannot be distinguished, in the ordinary complex, from those due to ammonia, but can be observed (Figure 1C, 3160 cm^{-1}) when $[Co(ND_3)_5N_3](ClO_4)_2$ is used as the starting material (see Experimental Section).

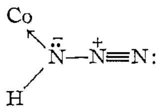
With respect to the protonation site, the reported spectral behavior indicates the most probable position. It is known that when N_3^- is coordinated to a metal cation the electronic distribution along the nitrogen chain is altered and the canonical structure II has a considerable weight, as demonstrated by the different N–N bond lengths[8] and by the shift of the antisymmetric mode toward higher frequencies with respect to the free azide ion.[9]

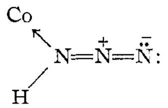

I


II

The protonation of coordinated N_3^- might occur, in principle, at both ends of the azide chain. On steric grounds, the nonbonded end may appear a more favorable site for the proton attack. However, it does not account for the spectral observations reported above. Thus, though the disappearance of the symmetric stretching could be attributed to the decrease of dipole moment, no explanation is found for the large shift toward higher frequencies observed for the antisymmetric mode.

If, instead, the protonation takes place at the coordinated nitrogen, then the bond orders of the two N–N oscillators become still more dissimilar since it must be expected that the mesomeric contribution of structure III be predominant over structure IV. On this ground the asymmetric and symmetric azide frequencies are expected to increase and decrease, respectively. The latter may well occur around 1100 cm^{-1} where it is masked by the strong broad ClO_4^- band (1050–1170 cm^{-1}).


III


IV

We conclude that the acidic product isolated may be regarded as $[Co(NH_3)_5NHN_2](ClO_4)_3$ containing a residue 10–15% of starting azide complex. This last may be responsible for the ir band still present at 2070 cm^{-1} (but of weaker intensity) in the spectra of Figure 1B and C.

On standing in air at room temperature, $[Co(NH_3)_5NHN_2](ClO_4)_3(s)$ undergoes a slow decomposition, indicated by the following observations. If an N_2 stream is bubbled through a fresh solution of an aged solid

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[6] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p 176, and references therein.

[7] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

[8] Y. Kushi, Y. Komiyama, and H. Kuruya, *Nippon Kagaku Zasshi*, **88**, 847 (1967).

[9] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, **78**, 3295 (1956).

sample, HN_3 is found in the gas and can be identified by the reaction with aqueous ferric chloride.[10]

The formation of free hydrazoic acid is also proved by the sharp band appearing at 2140 cm^{-1} in the ir spectrum of the solid.[11]

The titration of the HN_3-free solution of the partially decomposed complex shows the presence of both a strong and a weak acid. The pK_a of this latter is identical with that of $[Co(NH_3)_5OH_2](ClO_4)_3$, measured under similar conditions. As the decomposition proceeds, the molar ratio [strong acid]/[weak acid] decreases while the total acidity appears to be constant.

These observations indicate that the hydrazoic acid molecule tends to leave the coordination sphere. The appearance of a band at 3440 cm^{-1} in the ir spectrum of the aged samples suggests that HN_3 is replaced by atmospheric water. This interesting reaction is now under systematic investigation.

Experimental Section

Materials.—All reagents used were pure grade. Azidopentamminecobalt(III) chloride was prepared as described previously.[12] The perchlorate salt was prepared by dissolving the chloride in warm water and adding concentrated $HClO_4$ dropwise. The precipitate was then recrystallized twice from water.

Azidopenta(deuterio)amminecobalt(III) perchlorate was prepared by dissolving 1.0 g of the protic complex in 10 ml of 99.8% deuterium oxide, at 60°. After 10–15 min the solution was cooled in an ice bath and the precipitated complex was filtered off. This procedure was repeated in order to complete the deuteration. Finally, the deuterated complex was thoroughly washed with anhydrous ether. The protonated complex was prepared according to the following procedure. One gram of $[Co(NH_3)_5N_3](ClO_4)_2$ was dissolved in 200 ml of H_2O and the solution was cooled in an ice bath with stirring. About 500 ml of 70% $HClO_4$ was added dropwise to the solution. A pink-red precipitate was obtained while the remaining solution appeared colorless. The complex was filtered under dry nitrogen on a fritted-glass disk and thoroughly washed with anhydrous ether, until the washings gave a neutral reaction. The product was then dried under vacuum.[13]

A typical elemental analysis is reported in the text. This preparation was repeated several times with some changes in the reaction conditions but it was impossible to obtain the protonated complex with a 100% yield. Owing to its acid behavior it was also impossible to purify the mixture by means of the usual methods.

This compound was generally handled in small quantities without particular care. In one case, however, a sample exploded while it was being ground in a glass mortar.

The protonated complex containing deuterated ammonia was prepared according to the above procedure using $[Co(ND_3)_5N_3](ClO_4)_2$ as the starting material. The only difference was in the use of a slightly acidic solution ($HClO_4$) to dissolve the complex, in order to avoid the D–H exchange of the ammonia.

Spectra.—The ir and reflectance spectra were recorded with a Perkin-Elmer Model 237 spectrophotometer and with a Beckman DK 2 spectrophotometer, respectively.

Acknowledgments.—Professor A. Sabatini is gratefully thanked for very helpful discussions, concerning some aspects of the ir interpretation.

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[10] C. E. Roberson and C. M. Austin, *Anal. Chem.* **29**, 854 (1957).

[11] D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1258 (1955).

[12] M. Linhard and H. Flygare, *Z. Anorg. Chem.* **262**, 328 (1950).

[13] NOTE ADDED IN PROOF.—By a modification of the above reported procedure we succeeded in preparing a virtually pure sample of hydrazopentaamminecobalt(III) perchlorate, as demonstrated by the elemental analysis, the equivalent weight, and the ir spectrum. These results will be described in a following paper.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Hexakis(diethoxyphosphonylacetylmethano)trinickel[1]

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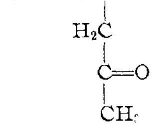
Several years ago the preparation of the ligand acid diethoxyphosphonylacetylmethane, I, and several complexes of the anion (DEPAM) were reported.[3] The pink cobalt(II) complex was of particular interest since the spectrum and magnetism indicated octahedral coordination while the molecular weight in freezing benzene corresponded to a trinuclear molecule. Moreover, increasing the temperature and/or decreasing the concentration of solutions caused the color to change from pink to, or toward, blue, suggesting dissociation to a tetrahedral monomer. It was considered plausible that the trimer might have a structure similar to that of hexakis(acetylacetonato)trinickel, shown schematically in Figure 1a. This structure preserves two chelate rings about each metal atom, and the equilibrium between such a trimer and the monomers is structurally straightforward. However, an X-ray study[4] revealed the structure shown schematically in Figure 1b, in which each terminal cobalt atom is tris-chelated and



$$\begin{array}{c}(C_2H_5O)_2P{=}O\\ |\\ H_2C\\ |\\ C{=}O\\ |\\ CH_3\end{array}$$

I

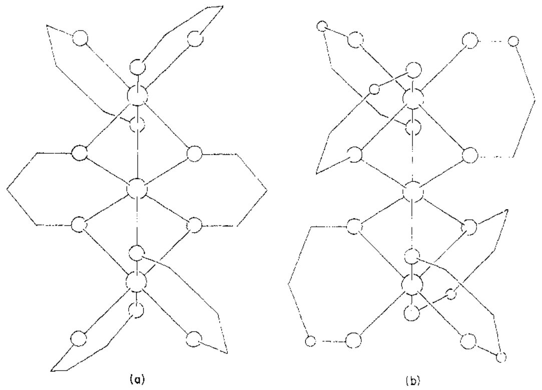


Figure 1.—(a) A schematic representation of bis(acetylacetonato)nickel(II). (b) A schematic representation of the structure of $\{[(C_2H_5O)_2P(O)CHCOCH_3]_2Co\}_3$. The small circles represent the phosphorus atom of the diethoxyphosphonylacetylmethanide anion, the medium circles are oxygen atoms, and the large circles are metal atoms.

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[1] Research supported by the National Science Foundation under Grant No. GP 7034X.

[2] National Institutes of Health Predoctoral Fellow, 1965–1968.

[3] F. A. Cotton and R. A. Schunn, *J. Amer. Chem. Soc.*, **85**, 2394 (1963).

[4] F. A. Cotton, R. Hügel, and R. Eiss, *Inorg. Chem.*, **7**, 18 (1968).