lows that the addition must have been more than 85% *cis*.

Since the reaction was rapid in the absence of light at −60°, and since styrene was found to add hydrogen bromide in the presence of acenaphthylene under identical conditions to give exclusively (2-bromoethyl)-benzene, the reaction cannot involve a radical mechanism. The identity of the styrene hydrobromide was established by n.m.r. analysis.

N.m.r. studies[7] confirm the above results. The bromide obtained from addition of deuterium bromide to acenaphthylene gives an n.m.r. spectrum with a complex multiplet extending from 2 τ to 3 τ, a doublet at 4.25 τ with a splitting of 7.4 c.p.s., and an unresolved broad signal at 6.15 τ. When this bromide is treated with lithium bromide in acetone, a significant change in the spectrum takes place. The signal at 4.25 τ becomes four lines of nearly equal intensity. The outer lines correspond with the original doublet while the inner lines are separated by 1.9 c.p.s.. Assignment of the 7.4 c.p.s. and 1.9 c.p.s. coupling to the *cis*- and *trans*-orientation of protons is consistent with the theoretical[8] and experimental[9] couplings found for dihedral angles of about 0° and 120°, respectively. Further verification is obtained when hydrogen bromide is added to the acenaphthylene containing >85% deuterium in the 1-position. The n.m.r. spectrum of the bromide in this case shows two strong lines at 4.25 τ separated by 1.9 c.p.s. Weak signals could also be detected corresponding to the 7.4 c.p.s. splitting.

It was possible to estimate from integrated peak intensities that no less than 85% of the *cis*-addition product was obtained. This is consistent with the results obtained from the elimination reaction. Similar results were obtained for addition reactions carried out in petroleum ether and pentane. We are currently investigating additions to other olefins and with other hydrogen halides in order to evaluate the various factors which determine the stereochemistry of the process.

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(9) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(10) National Science Foundation Predoctoral Fellow.

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RECEIVED MARCH 30, 1962

THE PREPARATION AND CHARACTERIZATION OF A COMPOUND CONTAINING TETRANITRATOCOBALTATE(II)

Sir:

We wish to report the preparation and characterization of a compound which is novel and interesting in two respects. The compound is tetramethylammonium tetranitratocobaltate(II), $[N(CH_3)_4]_2[Co(ONO_2)_4]$. This hygroscopic, violet compound was prepared by dissolving $[N(CH_3)_4]NO_3$ and $Co(No_3)_2\,2H_2O$ in 2:1 mole ratio in nitromethane. On addition of chloroform, the product separated in a crystalline state, and was filtered, washed with chloroform and dried in vacuum.

Anal. Calcd. for $C_8H_{24}CoN_6O_{12}$: C, 21.1; H, 5.3; N, 18.4. Found: C, 20.9; H, 5.5; N, 17.9.

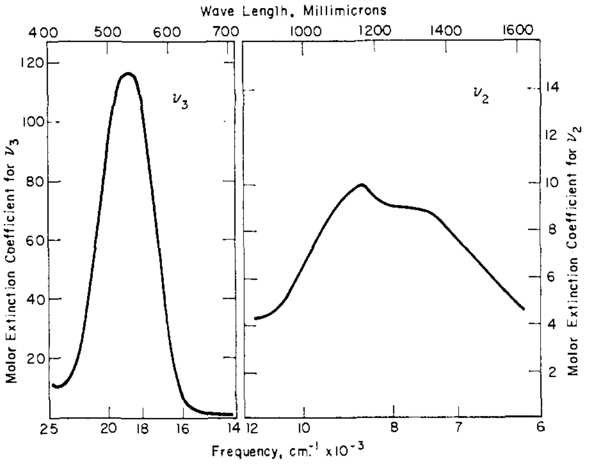

Fig. 1.—The visible and near infrared spectrum of $[N(CH_3)_4]_2[Co(ONO_2)_4]$, 0.01 molar, in acetonitrile containing 7.6×10^{-2} mole liter^{-1} of $[(C_6H_5)_3(n\text{-}C_4H_9)P]NO_3$. The mean energies of the absorption bands have been taken as 18,700 and 8,100 cm.$^{-1}$.

The infrared spectrum (mull) shows all of the bands characteristic of coördinated nitrate ions[1] (*i.e.*, M-ONO_2) and no others which cannot be assigned to the $[N(CH_3)_4]^+$ ions, thus supporting the view that all nitrate ions are coördinated to give $[Co(ONO_2)_4]^{2-}$ in the crystalline compound. There is also evidence that the same complex anions are present in acetonitrile solutions of the compound. Thus the molar conductance of a 0.003 molar solution in acetonitrile at 25° was 285 ohm^{-1} mole^{-1} which may be compared with a value of 266 ohm^{-1} mole^{-1} for a 0.003 molar solution of $[N(CH_3)_4]_2[Co(NCS)_4]$ in the same solvent. The infrared spectrum of a 0.1 molar solution in acetonitrile showed bands characteristic of coördinated nitrate ions. There were also very weak bands attributable to uncoördinated nitrate ions, indicating that slight dissociation of the complex anion occurs in this solvent.

The electronic absorption spectrum was recorded with successively increased additions of $[(C_6H_5)_3(n\text{-}C_4H_9)P]NO_3$ in order to repress dissociation of the complex anion. It was found that the spectra of 0.01 molar solutions in acetonitrile were identical for all phosphonium nitrate concentrations equal to or greater than 0.01 molar although the spectra of such solutions differed slightly, mainly in band intensities, from that of a solution containing only the cobalt compound. The spectrum is shown in Fig. 1.

The magnetic moment of $[N(CH_3)_4]_2[Co(ONO_2)_4]$ is 4.50 ±0.05 B.M. (calculated from susceptibility data with corrections for diamagnetism and temperature - independent paramagnetism[2]) which strongly implies[2] that the Co(II) is in a tetrahedral environment.

This compound is of interest since, to the best of our knowledge, it constitutes the first reasonably well-authenticated example of a compound con-

(1) B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(2) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

taining a polynitratometal ion, although it is not unlikely that others exist. It is to be noted that in his work on the preparation of anhydrous metal nitrates Addison[3] obtained a compound $Zn(NO_3)_2 \cdot N_2O_4$ for which he suggested the structure $(NO^+)_2[Zn(ONO_2)_4]$ and he also mentions isolating $Co(NO_3)_2 \cdot 2N_2O_4$ (red-purple) which is presumably of the same nature. It would appear worthwhile to attempt the preparation of other compounds containing $[M(ONO_2)_x]$ anions either by the simple method suggested here or by other metathetical reactions. However, we do not plan to undertake such studies in This Laboratory.

Our particular object in preparing this compound was to examine its spectral properties and electronic structure parameters. It recently has been shown[4] that there are tetrahedral complexes of Co(II) which have rather small decrements in the interelectronic repulsion parameter, B, and rather low electronic absorption band intensities. Since several of these are of the type $CoL_2(ONO_2)_2$ it seemed likely that the tetrahedral $[Co(ONO_2)_4]^{2-}$ ion should also have these properties. From the electronic spectrum we obtain[2] $\Delta = 4660$ cm.$^{-1}$, $B = 855$ cm.$^{-1}$ and $f(\nu_3) = 1.94 \times 10^{-3}$. Thus on the previously reported plot of ΔB *vs.* $f(\nu_3)$,[5] the point for $[Co(ONO_2)_4]^{2-}$ falls very close to the best line through the points for the other compounds. It is also interesting that the Δ value places the nitrate ion further toward the strong end of the spectrochemical series than are other oxygen-coördinating ligands.

We are grateful to the U. S. Atomic Energy Commission and the Alfred P. Sloan Foundation for financial aid.

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(3) C. C. Addison and B. J. Hathaway, "Recent Aspects of the Inorganic Chemistry of Nitrogen," the Chemistry Society, London, Special Publication No. 10, 1957, p. 41.

(4) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962).

(5) $\Delta B = 967 - B$.

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RECEIVED MARCH 31, 1962

TETRAHEDRAL COMPLEXES CONTAINING NITROGEN-TO-NICKEL BONDS[1]

Sir:

We are unaware of any evidence previously reported for a tetrahedral configuration for solid complexes containing nitrogen-to-nickel bonds. The infrared spectrum of dark green diiodobis-(pyridine)-nickel(II) was observed to be characteristic of tetrahedral compounds of the type Mpy_2X_2, particularly in the position of the absorption associated with the C–H in-plane bending vibration at 1068 cm.$^{-1}$ and the splitting (755 and 753 cm.$^{-1}$) associated with coupling between C–H out-of-plane bending vibrations in adjacent pyridine rings. A typical splitting also was observed in the 700 cm.$^{-1}$ region, with peaks at 693 and 689 cm.$^{-1}$. The spectrum differed in these respects from those of the bridged, octahedral dichloro and dibromo complexes. The visible and near infrared spectra in a potassium bromide disk and benzene solution revealed absorption in the 600 and 900 mμ regions characteristic of tetrahedral nickel(II) complexes. The absorption maxima in millimicrons observed in benzene solution (molar extinction coefficients in parentheses) are: 405(2060), 455(2220), 575(320), 925(90), and 1000(110). A magnetic moment of 3.44 Bohr magnetons was obtained for the solid. This is lower than the values reported for NiX_4^{-2} anions,[2] and for tetrahedral $((C_6H_5)_3PO)_2NiX_2$ and $((C_6H_5)_3AsO)_2NiX_2$ complexes,[3] but higher than the values reported for the tetrahedral $((C_6H_5)_3P)_2NiX_2$ compounds.[4] Diiodobis-(pyridine)-nickel(II) was prepared by refluxing a mixture of anhydrous nickel(II) iodide and pyridine for eight hours. The excess pyridine was decanted and the solid product washed with boiling alcohol. A light green solid, diiodotetra-(pyridine)-nickel(II) separated from the alcohol on cooling. This was heated at 110° in an Abderhalden apparatus until the uniform dark green product was obtained. *Anal.* Calcd. for $C_{10}H_{10}I_2NiN_2$: Ni, 12.47; I, 53.92. Found: Ni, 12.65; I, 53.56.

Diiodobis-(β-picoline)-nickel(II) was prepared in a similar manner, except that the reaction mixture was refluxed only 30 minutes. After decanting the excess picoline, the light green tetrapicoline complex was washed with petroleum ether before converting to the dark green bispicoline complex by heating. The tetrahedral configuration of this compound is indicated by the similarity of its infrared spectra with that of the corresponding blue cobalt(II) complex and by its visible and near infrared spectra in KBr and benzene solution. The absorption maxima in benzene are 405 mμ (2040), 462(2060), 585(300), 925(90) and 1000(100). A value of 3.21 was obtained for the magnetic moment of the solid. *Anal.* Calcd. for $C_{12}H_{14}I_2NiN_2$: C, 28.90; H, 2.83. Found: C, 28.27; H, 3.47.

It was expected that steric effects would prevent halogen bridging in the bis complexes of α-picoline with $NiCl_2$ and $NiBr_2$. This appears to be the case. These compounds are dark blue, indicating that they are tetrahedral. Solid dichlorobis-(α-picoline)-nickel(II) absorbs at 555 and 950 mμ (weak) and has a magnetic moment of 3.3. Solid dibromobis-(α-picoline)-nickel(II) absorbs at 562 and 950 mμ (weak) and has a magnetic moment of 3.35. The dibromo complex was prepared by refluxing anhydrous nickel bromide in an excess of α-picoline for 30 minutes. The excess ligand was removed under vacuum and the product washed several times with petroleum ether and then dried over phosphoric anhydride. It could not be recrystallized as it decomposes in the usual solvents. *Anal.* Calcd. for $C_{12}H_{14}Br_2NiN_2$: Ni, 14.26; C, 35.60; H, 3.47. Found: Ni, 14.15; C, 34.36; H, 4.17. The dichloro compound was prepared by adding equivalent portions of nickel(II) chloride hexahydrate and α-picoline to absolute ethanol. After considerable stirring the mixture was placed in a vacuum desiccator over sulfuric acid for several

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(1) Supported in part under AEC Contract AT(11-1)-38, Radiation Laboratory of the University of Notre Dame.

(2) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(3) D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **82**, 5774 (1960).

(4) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *ibid.*, **83**, 344 (1961).