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.

(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.
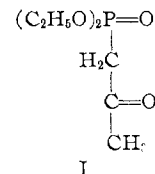
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS 02139

Hexakis(diethoxyphosphonylacetylmethano)trinickel[1]

BY F. A. COTTON AND B. H. C. WINQUIST[2]

Several years ago the preparation of the ligand acid diethoxyphosphonylacetylmethane, I, and several com-

$$(C_2H_5O)_2P{=}O$$
$$H_2C$$
$$C{=}O$$
$$CH_3$$
$$I$$

plexes 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
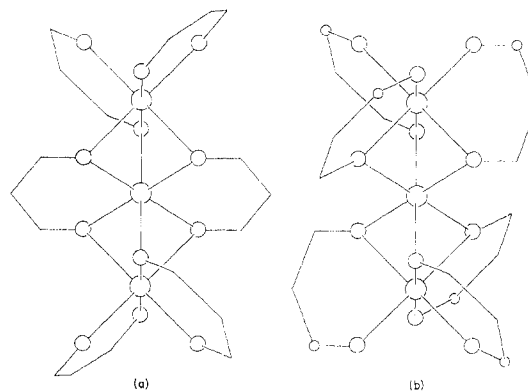

Figure 1.—(a) A schematic representation of bis(acetylacetonato)nickel(II). (b) A schematic representation of the structure of $\{[(C_2H_5O)_2P(O)CHCOCH_3]_2Co\}_3$. The small circles represent the phosphorus atom of the diethoxyphosphonylacetylmethanide anion, the medium circles are oxygen atoms, and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

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

(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).

the central one is not part of any chelate ring. We report here the preparation and characterization of the nickel(II) complex of DEPAM and some further observations on the cobalt compound.

Experimental Section

General.—All manipulations were performed in an atmosphere of dry, prepurified nitrogen except for some transfers which were carried out rapidly under a flow of nitrogen to reduce contact with air and moisture. Toluene, *m*-xylene, and benzene were refluxed over sodium for 4 hr prior to distillation and storage under nitrogen. Tetrahydrofuran (THF) was refluxed over Li-AlH₄ and distilled immediately before use. Reagent grade anhydrous ether and petroleum ether (bp 60–80°) were used from freshly opened containers.

Diethoxyphosphonylacetylmethanosodium and Bis(diethoxyphosphonylacetylmethano)cobalt(II).—$[(C_2H_5O)_2P(O)CHCO-CH_3]Na$ and $[(C_2H_5O)_2P(O)CHCOCH_3]_2Co$ were prepared according to the procedure of Cotton and Schunn.[3]

Bis(diethoxyphosphonylacetylmethano)nickel(II).—This compound was prepared by a modification of the procedure for Co(DEPAM)₂. To a magnetically stirred slurry of 1.51 g (6.91 mmol) of NiBr₂ in 80 ml of tetrahydrofuran, prepared by extraction of commercial anhydrous NiBr₂ (Alfa Inorganics, Inc.) with a Soxhlet extractor, was added dropwise a solution of 3.58 g (16.6 mmol) of diethoxyphosphonylacetylmethanosodium[5] in 40 ml of THF. The solution became turbid immediately and turned green when addition was complete. After the mixture had been stirred for 2 hr the NaBr was filtered off with a fine frit and the resulting solution evaporated at reduced pressure to a thick green syrup. The syrup was dissolved in 35 ml of toluene, the solution was filtered, and the toluene was evaporated at room temperature. Addition of 15 ml of ether and cooling to −80° for 2 days produced 0.93 g (30%) of pale green crystals. *Anal.* Calcd for C₁₄H₂₈NiO₈P₂: C, 37.78; H, 6.34; P, 13.92. Found: C, 38.0; H, 6.30; P, 14.1.

The compound is a slightly hygroscopic green crystalline solid, soluble in toluene, THF, xylene, and benzene, slightly soluble in ether, and insoluble in pentane.

Visible Spectra.—The spectrum of a solution of Co₃(DEPAM)₆ in *m*-xylene was measured on a Beckman DU spectrophotometer with a variable-temperature cell compartment of local design. Solutions were prepared by vacuum distillation of dry solvent onto the solid in a cylindrical cell. The cell was sealed off under vacuum to prevent exposure to air and loss of solvent when the spectrum was run at elevated temperature. Instability of the electronic circuitry of the spectrophotometer at high temperature and the use of cylindrical cells precluded accurate measurement of the molar extinction coefficients, but the shape of the spectrum was reproducible and is believed to be correct. The spectra at 28 and 79° are shown in Figure 2. Similar study of the nickel compound revealed no significant spectral changes from 25 to 80°.

X-Ray Investigation of Bis(diethoxyphosphonylacetylmethano)-nickel(II).—Crystals suitable for X-ray photography were obtained by cooling an ether solution of Ni(DEPAM)₂ at −80° for 48 hr. A monoclinic prism was mounted on a glass fiber and coated with a thin film of shellac to prevent exposure to the atmosphere. Weissenberg and precession photography of the *h0l*, *h1l*, *h2l*, and *hk0* levels of the reciprocal lattice using Ni-filtered Cu Kα radiation revealed diffraction symmetry 2/m and the systematic extinctions *h0l*, *l* ≠ 2*n*, and *0k0*, *k* ≠ 2*n*, uniquely determining the space group P2₁/c (no. 14, C_{2h}^5). Cell constants measured from Weissenberg films were *a* = 11.18 ± 0.02 Å,

(5) Successful preparation of this intermediate requires attention to several points. (1) Because iodoacetone polymerizes readily, it should be used as soon as possible after it is prepared. If it must be kept overnight, it should be stored at −80°. (2) Diethoxyphosphonylacetylmethane is sensitive to air and light and should be treated with the proper amount of sodium sand *immediately* after distillation. (3) The extremely hygroscopic sodium salt is more stable but becomes yellow after standing a few weeks, even if air and moisture are rigorously excluded.
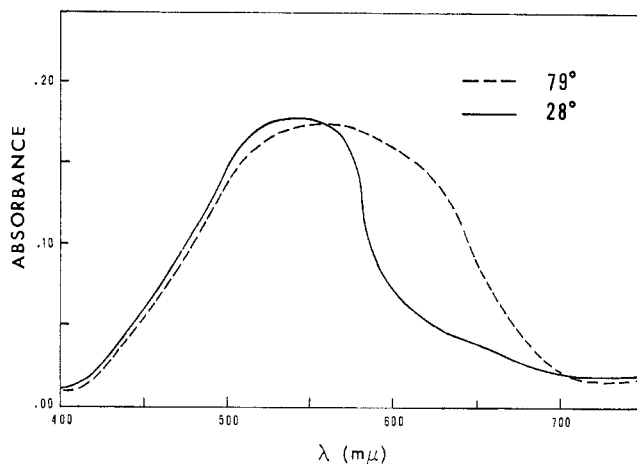
Figure 2.—The visible spectrum of a 0.013 *M* solution of [(C₂-H₅O)₂P(O)CHCOCH₃]₂Co in *m*-xylene at 28° and 79°.

b = 12.75 ± 0.03 Å, *c* = 24.25 ± 0.11 Å, and *β* = 115° 12′ ± 12′. The density measured by flotation in a mixture of carbon tetrachloride and heptane was 1.41 ± 0.01 g/cm³. The density calculated for Z = 2 (trimeric) molecules per unit cell is 1.42 g/cm³. The intensities on an upper level Weissenberg photograph were compared visually with similar photographs of Co₃(DEPAM)₆.

Discussion

Co₃(DEPAM)₆.—The original observation of temperature-dependent color changes in solutions of Co₃(DEPAM)₆ was confirmed by these investigations, as shown by the spectra in Figure 2. Solutions in *m*-xylene and tetrachloroethylene, pink at room temperature, when heated to 80° change to a violet-pink and at 140° are deep blue. This change is reversible and has been repeated as many as 10 times without any indication of decomposition. With available equipment, the spectrum could be recorded only up to ∼80°.

As shown in Figure 2, the room-temperature spectrum (28°) has as its principal feature an absorption band with a maximum at ∼550 mμ accounting for the pink color, whereas at 79°, at which temperature the solution is violet-pink, there is a broader band, centered at ∼570 mμ. The spectral changes seen in Figure 2 are consistent with the conversion of a small percentage of the trimer to tetrahedral monomers at ∼80°, bearing in mind the typical positions and intensities of the ⁴T₁g(F) → ⁴T₁g(P) transition of octahedral Co(II) and the ⁴A₂ → ⁴T₁(P) transition of tetrahedral Co(II).[6]

Ni₃(DEPAM)₆.—Comparison of crystallographic data from Co₃(DEPAM)₆ and Ni₃(DEPAM)₆ indicate conclusively that the two compounds have identical structures. Both compounds crystallize forming monoclinic prisms of similar habits and of equal densities (*d*obsd for Co₃(DEPAM)₆ and Ni₃(DEPAM)₆ are 1.40 and 1.41 g/cm³, respectively). The space group of both compounds is P2₁/c and the unit cell dimensions for the cobalt and nickel compounds are, respectively: *a* = 11.203 ± 0.005, *b* = 12.825 ± 0.010, *c* = 23.945 ± 0.010 Å, *β* = 114.48 ± 0.05°; and *a* = 11.18 ± 0.02,

(6) *Cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Division, John Wiley and Sons, New York, N. Y., 1966, pp 870–872.

$b = 12.75 \pm 0.03$, $c = 24.25 \pm 0.11$ Å, $\beta = 115.20 \pm 0.20°$. The $h1l$ level Weissenberg photographs taken of both compounds, each mounted along the b crystallographic axis, were virtually indistinguishable in terms of reflection positions and intensities. Thus, the remarkable structure found for $Co_3(DEPAM)_6$ occurs also for $Ni_3(DEPAM)_6$. The latter appears to be

somewhat more stable relative to monomers. Although a solution of $Ni_6(DEPAM)_6$ in m-xylene, which is green at 25°, turns straw-colored and then light brown at temperatures from 100 to 150°, the spectrum at 80° did not differ significantly from that at room temperature. The observed color changes were reversible.

Correspondence

Evaluation of Dipolar Nuclear Magnetic Resonance Shifts

Sir:

The magnetic resonances of nuclei in paramagnetic complexes often show large isotropic shifts from their diamagnetic positions.[1] These shifts are of two types: contact shifts resulting from the presence of unpaired electron spin density at the resonating nucleus and dipolar shifts caused by a dipolar interaction between the electronic magnetic moment and the nuclear spin which does not vanish in magnetically anisotropic systems. It is the purpose of this article to clarify one method of separating observed isotropic shifts $\Delta\nu^{iso}$ into dipolar $\Delta\nu^{dip}$ and contact $\Delta\nu^{con}$ contributions, and to discuss its application to a system wherein it had been reported to fail.[2] The direct evaluation of dipolar shifts from single-crystal magnetic anisotropy data will also be discussed and applied to the case at hand.

It is possible to separate dipolar and contact contributions to observed isotropic shifts if it can be established, for two series of complexes differing only in central metal ion, that the modes of spin delocalization are identical and that one member is magnetically isotropic (*i.e.*, exhibits no dipolar shifts). This procedure, which will be referred to here as the ratio method, has been applied with apparent success by the present author and his coworkers[3-6] on several occasions and by others[7] to parallel series of magnetically isotropic[8] six-coordinate nickel(II) and magnetically anisotropic[8] cobalt(II) complexes, although the underlying assumptions and limitations of the method were perhaps not properly enunciated at the time. The basic assumption of the method is the following: if the unpaired spin is delocalized in a particular ligand molecular orbital, then it will be distributed according to the MO coefficients of the orbital involved. Only a small change in ligand electronic structure is to be expected when the metal is changed. Cobalt and nickel

differ by a single nuclear charge and single extranuclear electron. The quantity of unpaired spin delocalized in a particular MO may be different for cobalt and nickel, say, but the pattern of distribution should be the same. In other words the *ratios* of *contact* shifts for systems differing only in the metal should be identical. This may be expressed quantitatively by eq 1,

$$\frac{\Delta\nu_{Co}^{con}(i)}{\Delta\nu_{Co}^{con}(j)} = \frac{\Delta\nu_{Ni}^{con}(i)}{\Delta\nu_{Ni}^{con}(j)} = \frac{\Delta\nu_{Co}^{iso}(i) - \Delta\nu_{Co}^{dip}(i)}{\Delta\nu_{Co}^{iso}(j) - \Delta\nu_{Co}^{dip}(j)} \quad (1)$$

where i and j refer to the ith and jth sets of equivalent ligand nuclei. Since dipolar shifts are absent for octahedral nickel(II), $\Delta\nu_{Ni}^{con}(i) = \Delta\nu_{Ni}^{iso}(i)$. For the axially symmetric systems of interest here the dipolar shift of the ith proton resonance is given by eq 2,[9-11]

$$\frac{\Delta\nu_{(i)}^{dip}}{\nu} = -DG(\chi,r)_i \quad (2)$$

where ν is the spectrometer frequency and D is a function of temperature and the magnetic properties of the complex[12] (*vide infra*). The geometric factor $G(\chi,r)_i$ is given by eq 3.[9] Here r_i is a vector from the cobalt atom to the ith nucleus and χ_i is the angle made by this vector with the symmetry axis. The average is taken over nuclear motions which are rapid on the nmr time scale. Dipolar shifts in a given complex may thus be expressed in terms of the shift for a particular nucleus and ratios of geometric factors. Let X_0 be the dipolar shift for the standard nucleus (0); then the dipolar shifts for all the other nuclei are given by

$$G(\chi,r)_i = \left\langle \frac{3\cos^2\chi_i - 1}{r_i^3} \right\rangle_{av} \quad (3)$$

$$\Delta\nu_{Co}^{dip}(i) = R(i)X_0 \quad (4)$$

where

$$R(i) = \frac{G(\chi,r)_i}{G(\chi,r)_0} \quad (5)$$

is the ratio of the ith geometric factor to that of the standard.

Equation 1 becomes

$$\frac{\Delta\nu_{Ni}^{iso}(i)}{\Delta\nu_{Ni}^{iso}(0)} = \frac{\Delta\nu_{Co}^{iso} - R(i)X_0}{\Delta\nu_{Co}^{iso}(0) - X_0} \quad (6)$$

(1) For a review see D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965).

(2) M. L. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 2196 (1968).

(3) W. DeW. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *ibid.*, **86**, 3031 (1964).

(4) R. W. Kluiber and W. DeW. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

(5) R. W. Kluiber and W. DeW. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

(6) R. W. Kluiber and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **6**, 166 (1967).

(7) E. E. Zaev and Y. N. Molin, *J. Struct. Chem.*, **7**, 639 (1966).

(8) B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).

(9) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(10) J. P. Jesson, *ibid.*, **47**, 579 (1967).

(11) J. P. Jesson, *ibid.*, **47**, 582 (1967).

(12) D of eq 2 corresponds to the D of ref 11 divided by ν.