Scheme I

$$[PtCl_2(PPh_3)_2] + SnCl_2 \rightleftharpoons [Pt(SnCl_3)Cl(PPh_3)_2]$$

$$[Pt(SnCl_3)Cl(PPh_3)_2] + H_2 \rightleftharpoons [PtH(SnCl_3)(PPh_3)_2] + H^+ + Cl^-$$

$$SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-$$

$$SnCl_3^- + H^+ \rightleftharpoons HSnCl_3$$

$$[PtH(SnCl_3)(PPh_3)_2] + \text{olefin} \longrightarrow [PtH(SnCl_3)(\text{olefin})(PPh_3)_2]$$
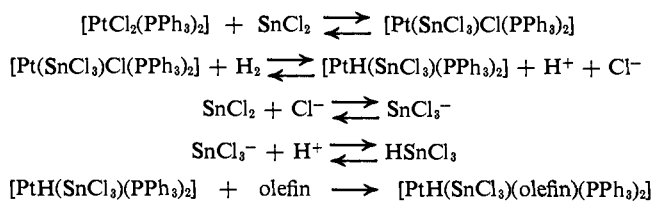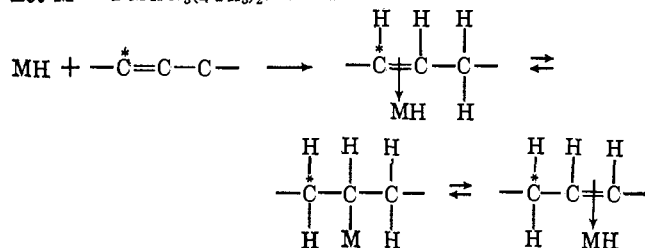
Let $M = PtSnCl_3(PPh_3)_2$. Thus

may be of a transitory existence because the metal-carbon bond is weak in this complex because of the lack of back electron donation and π bonding. It therefore rearranges to a hydridometal–olefin complex by the abstraction by the metal atom of a hydrogen atom, possibly from a location that leads to double-bond migration. These processes may be repeated several times. At some stage in the process, the isomerized coordinated olefin exchanges with the unisomerized olefin in solution. Exchange reactions continue, and an equilibrium mixture of isomers is obtained. In dienes, conjugated isomers are expected to be the major isomerization products since they are stabilized by resonance relative to the nonconjugated isomers.

The Structure of a Trigonal-Bipyramidal Nickel(II) Cyanide Complex Containing the Tetradentate Ligand Tris(3-dimethylarsinopropyl)phosphine

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Abstract: A structural determination of [Ni(TAP)CN$^+$]ClO$_4^-$ (where TAP = tris(3-dimethylarsinopropyl)phosphine) was undertaken in order to study the coordination of a tetradentate ligand to a Ni(II) atom. This complex crystallizes with four formula species in an orthorhombic unit cell of symmetry $P2_12_12_1$ and of dimensions $a = 10.27$ A, $b = 14.04$ A, and $c = 17.79$ A. The configuration of the idealized cation, [Ni(TAP)CN$^+$], is a trigonal bipyramid in which the central nickel atom is surrounded by three arsenic atoms at equatorial sites and a phosphorus atom and a cyanide group in apical positions; each arsenic atom is connected to the apical phosphorus atom by a trimethylene chain such that the cation possesses a pseudo-threefold axis. The absolute conformation of the cation in the crystal examined was determined from anomalous dispersion effects.

I$\quad$n recent years a substantial number of five-coordinate Ni(II) complexes which contain mono-, bi-, tri-, or tetradentate donor ligands comprised of nitrogen, phosphorus, sulfur, or arsenic atoms have been synthesized and characterized both by chemical and physical means.[2-8] One such series of Ni(II) complexes possessing a mixed arsenic–phosphorus donor system was prepared by Benner, Hatfield, and Meek[5] through the reaction of nickel(II) salts with tris(3-dimethylarsinopropyl)phosphine (TAP). Five-coordinate metal cations of general formula [Ni(TAP)X$^+$] (where X = Cl,

Br, NO$_2$, CN, SCN, or SC$_2$H$_5$) were postulated by these workers from magnetic susceptibility, electronic absorption, and conductivity measurements. Although stereochemical considerations indicate that the tetradentate ligand TAP can coordinate to four of the five bonding sites of either a square-pyramidal or trigonal-bipyramidal configuration, Meek and co-workers[5] assigned a trigonal-bipyramidal structure to the diamagnetic [Ni(TAP)X$^+$] cations on the basis of the close similarity of their electronic spectra to those of the [Ni(QAS)X$^+$] and [Pt(QAS)I$^+$] cations (where QAS = tris(o-diphenylarsinophenyl)arsine); the platinum complex had been previously shown by an X-ray structural determination[9] to possess a trigonal-bipyramidal configuration. A single-crystal X-ray diffraction study of [Ni(TAP)CN$^+$]ClO$_4^-$ was undertaken not only to determine the over-all configuration and thereby to establish which of the three possible geometrical isomers of a trigonal-pyramidal cation is actually formed but also to obtain

(1) This paper is based in part on a dissertation submitted by D. L. Stevenson to the Graduate Schoool of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1967.

(2) G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953).

(3) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

(4) R. G. Hayter, *Inorg. Chem.*, 2, 932 (1963).

(5) G. S. Benner, W. E. Hatfield, and D. W. Meek, *ibid.*, 3, 1544 (1964).

(6) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

(7) G. Dyer and D. W. Meek, *Inorg. Chem.*, 4, 1398 (1965).

(8) M. Ciampolini and N. Nardi, *ibid.*, 5, 41 (1966).

(9) G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961).

structural details for a trigonal-bipyramidal Ni(II) system.

Experimental Section

Dark red crystals of [Ni(TAP)CN$^+$]ClO$_4^-$ were generously supplied to us by Professor Devon Meek of the Ohio State University. Preliminary X-ray examination of a number of crystals enclosed in Lindemann thin-walled glass capillaries was made; for the collection of intensity data an approximately cylindrical crystal of length 0.5 mm and average width 0.25 mm mounted around the needle axis was used. Lattice lengths were measured from $hk0$ and $h0l$ precession photographs which were calibrated by the superimposing of a zero-layer NaCl exposure on the same films.

Multiple-film equiinclination Weissenberg photographs of reciprocal levels $0kl$ through $8kl$ and timed sets of precession photographs of reciprocal levels $hk0$, $hk1$, $h0l$, $h1l$, and $h2l$ were taken with Zr-filtered Mo Kα radiation. The intensities of all reflections were estimated by visual comparison with timed sets of standard intensities prepared from the same crystals. After the usual corrections for Lorentz-polarization effects and spot extension,[10] the Weissenberg and precession data were merged via least squares[11] to give a total of 1150 independent diffraction maxima. The low weighted reliability index of 4.0% indicates that little systematic error was introduced into the data by the merging process.

Standard deviations of the structure amplitudes were assigned according to the following equations.[12]

If $(hkl) \geqslant \sqrt{10}$

$$\sigma[F_o(hkl)] = F_o(hkl)/20$$

If $(hkl) < \sqrt{10}$

$$\sigma[F_o(hkl)] = [F_o(hkl)/20][\sqrt{10}I_{min}/I_o(hkl)]^2$$

Atomic scattering factors for all atoms were taken from the Hartree–Fock–Slater calculations of Hanson, et al.[13] The real and imaginary anomalous contributions to the scattering factors of the arsenic and nickel atoms were obtained from those compiled by Templeton.[14]

Crystal Data

Crystals of [Ni(TAP)CN$^+$]ClO$_4^-$ (mol wt 656.4) are orthorhombic with $a = 10.27 \pm 0.02$ A, $b = 14.04 \pm 0.02$ A, and $c = 17.79 \pm 0.02$ A; volume of the unit cell $= 2565$ A^3; $\rho_{obsd} = 1.70$ g/cc vs. $\rho_{calcd} = 1.70$ g/cc for four molecules per unit cell. The total number of electrons per unit cell, $F(000)$, is 1320. The linear absorption coefficient for Mo Kα radiation is 50 cm^{-1}. Systematic absences of $h = 2n + 1$ for $\{h00\}$, $k = 2n + 1$ for $\{0k0\}$, and $l = 2n + 1$ for $\{00l\}$ indicate P2$_1$2$_1$2$_1$ (D$_2^4$) as the probable space group. This noncentrosymmetric space group, which was confirmed by successful refinement of the structure, requires all atoms to be in a fourfold set of general positions:[15] $(x, y, z; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$. Thus, the structural analysis necessitates the location of 27 nonhydrogen atoms corresponding to one formula unit.

Solution of the Structure

An interpretation of the Harker sections of a three-dimensional Patterson function yielded the positional

(10) D. C. Phillips, Acta Cryst., 7, 746 (1954).

(11) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1964.

(12) D. L. Smith, "DACOR—A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

(13) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, Acta Cryst., 17, 1040 (1964).

(14) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(15) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 105.

Table I. Final Atomic Parameters with Standard Deviations

| Atom	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
As(1)	0.9355(3)	0.3875(3)	0.3850(2)	...[a]
As(2)	0.7277(3)	0.6100(2)	0.4586(2)	...[a]
As(3)	0.5499(3)	0.3890(3)	0.3563(2)	...[a]
Ni	0.7399(4)	0.4695(2)	0.3910(2)	...[a]
P	0.7656(8)	0.5412(5)	0.2816(4)	1.9(1)
N	0.7197(22)	0.3745(19)	0.5414(15)	4.2(6)
C(1)	1.0639(31)	0.4136(22)	0.3052(15)	3.7(7)
C(2)	0.9941(28)	0.4392(24)	0.2302(15)	3.5(7)
C(3)	0.9254(26)	0.5413(21)	0.2408(14)	2.5(6)
H$_3$C(4)	0.9121(36)	0.2471(34)	0.3887(22)	6.0(9)
H$_3$C(5)	1.0536(30)	0.4131(22)	0.4725(16)	3.9(7)
C(6)	0.6963(32)	0.7350(25)	0.4094(20)	4.7(9)
C(7)	0.7832(33)	0.7384(25)	0.3357(21)	5.1(8)
C(8)	0.7207(26)	0.6696(19)	0.2727(15)	2.6(6)
H$_3$C(9)	0.8788(31)	0.6355(28)	0.5221(19)	5.1(9)
H$_3$C(10)	0.5854(28)	0.6177(29)	0.5337(16)	4.2(7)
C(11)	0.4693(26)	0.3992(23)	0.2565(14)	2.8(6)
C(12)	0.5158(28)	0.4918(23)	0.2166(16)	3.6(7)
C(13)	0.6780(26)	0.4908(21)	0.2023(15)	2.9(6)
H$_3$C(14)	0.3976(36)	0.4182(28)	0.4180(21)	6.3(10)
H$_3$C(15)	0.5694(38)	0.2473(34)	0.3644(20)	6.1(10)
C(16)	0.7229(25)	0.4089(18)	0.4844(14)	2.3(6)
Cl	1.2587(9)	0.6674(6)	0.3320(5)	4.2(2)
O(1)	1.1788(35)	0.6409(28)	0.3938(21)	11.9(11)
O(2)	1.2088(34)	0.7580(26)	0.3015(20)	11.1(10)
O(3)	1.3941(29)	0.6773(25)	0.3519(17)	8.9(8)
O(4)	1.2526(25)	0.5975(15)	0.2741(12)	5.6(5)

[a] The arsenic and nickel atoms were refined using anisotropic temperature factors of the form $\exp\{-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23})\}$; the resulting thermal coefficients with the standard deviations of the last significant figures are listed below.

Atom	$10^4 B_{11}$	$10^4 B_{22}$	$10^4 B_{33}$	$10^4 B_{12}$	$10^4 B_{13}$	$10^4 B_{23}$
As(1)	65(4)	44(2)	22(1)	13(2)	4(1)	11(2)
As(2)	79(4)	37(2)	17(1)	−7(3)	1(1)	−5(2)
As(3)	58(4)	41(2)	22(1)	−16(3)	−2(1)	5(2)
Ni	52(4)	32(2)	10(1)	−3(3)	2(2)	5(1)

parameters of the nickel and three arsenic atoms. The other nonhydrogen atoms were located from successive three-dimensional Fourier maps. A full-matrix, least-squares refinement, in which a single scale factor was used for all data and in which anisotropic temperature factors were utilized for the nickel and arsenic atoms, gave final discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 6.9\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2]^{1/2} \times 100 = 7.5\%$. A final three-dimensional Fourier difference map based on the observed and calculated structure factors obtained from the last refinement cycle showed no residual electron-density peak greater than 1.2 e/A^3 or less than −1.1 e/A^3. No attempt was made to identify any of the positive peaks as hydrogen atoms.

The positional and thermal parameters from the final mixed anisotropic-isotropic refinement cycle are given in Table I.[16] In order to verify the over-all correctness of the structure, unobserved but experimentally accessible data (i.e., those reflections either too weak to be judged or actually unobserved) for which sin $\theta \leq 0.43$ were assigned an intensity equal to the minimum observed intensity for the given reciprocal level. After correction of these intensities for Lorentz-polarization effects and spot extension, a comparison of the derived

(16) Calculated and observed structure factors for [Ni(TAP)CN$^+$]-ClO$_4^-$ are deposited as Document No. 9419 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief: Photoduplication Service, Library of Congress.

$$\left[\text{Ni} \left\{ [(CH_3)_2 As(CH_2)_3]_3 P \right\} (CN) \right]^+$$
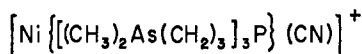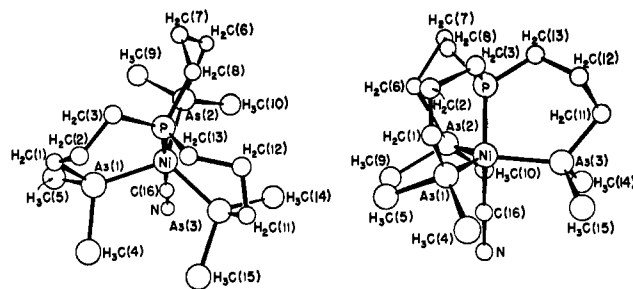
Cyanotris(3-dimethylarsinopropyl)phosphinenickel (Ⅱ) Cation

Figure 1. Configuration of the [Ni(TAP)CN$^+$] cation of pseudo-C_3 symmetry.

structure factors with the corresponding calculated ones showed that no F_c exceeded $1.5F_o$(min). The bond lengths and angles with their standard deviations, grouped according to the C_3 symmetry of the idealized cation and the T_d symmetry of the idealized anion, are given in Tables II and III, respectively.

Table II. Bond Lengths (A) with Standard Deviations[a]

As(1)–Ni	2.317 (6)	C(3)–P	1.79 (3)
As(2)–Ni	2.313 (5)	C(8)–P	1.87 (3)
As(3)–Ni	2.338 (6)	C(13)–P	1.82 (3)
	2.322 (3)		1.83 (2)
		As(1)–H$_3$C(4)	1.99 (5)
Ni–P	2.206 (8)	As(2)–H$_3$C(9)	1.96 (3)
Ni–C(16)	1.87 (3)	As(3)–H$_3$C(14)	1.95 (4)
C(16)–N	1.12 (3)		1.96 (3)
As(1)–C(1)	1.97 (3)		
As(2)–C(6)	1.99 (4)	As(1)–H$_3$C(5)	2.01 (3)
As(3)–C(11)	1.97 (3)	As(2)–H$_3$C(10)	1.98 (3)
	1.97 (2)	As(3)–H$_3$C(15)	2.00 (5)
			2.00 (3)
C(1)–C(2)	1.56 (4)	Cl–O(1)	1.42 (4)
C(6)–C(7)	1.59 (4)	Cl–O(2)	1.48 (4)
C(11)–C(12)	1.55 (4)	Cl–O(2)	1.44 (3)
	1.57 (2)	Cl–O (4)	1.42 (2)
			1.44 (1)
C(2)–C(3)	1.61 (4)		
C(7)–C(8)	1.61 (4)		
C(12)–C(13)	1.68 (4)		
	1.64 (2)		

[a] The standard deviations of the last significant figures are enclosed in parentheses.

The three-dimensional Patterson and Fourier maps were calculated with the Blount program.[17] A local version of the Busing–Martin–Levy ORFLS program[18a] was used to carry out the full-matrix, least-squares refinement cycles. Bond lengths and angles with their standard deviations were obtained from the inverse matrix (which included estimated errors in the lattice lengths) with the Busing–Martin–Levy ORFFE program.[18b] The "best" molecular planes determined by

(17) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(18) (a) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS—A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963; (b) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

Table III. Bond Angles (Degrees) with Standard Deviations[a]

As(1)–Ni–As(2)	119.6 (2)	C(3)–P–C(8)	101.0 (13)
As(2)–Ni–As(3)	120.3 (2)	C(3)–P–C(13)	97.9 (13)
As(3)–Ni–As(1)	118.1 (2)	C(8)–P–C(13)	100.8 (13)
	119.3 (1)		99.9 (8)
As(1)–Ni–P	94.7 (2)	H$_3$C(4)–As(1)–Ni	112.7 (11)
As(2)–Ni–P	94.4 (2)	H$_3$C(9)–As(2)–Ni	114.4 (11)
As(3)–Ni–P	95.0 (2)	H$_3$C(14)–As(3)–Ni	114.7 (12)
	94.7 (1)		114.0 (7)
As(1)–Ni–C(16)	84.0 (8)	H$_3$C(5)–As(1)–Nii	113.6 (9)
As(2)–Ni–C(16)	85.5 (8)	H$_3$C(10)–As(2)–N	115.9 (12)
As(3)–Ni–C(16)	86.4 (8)	H$_3$C(15)–As(3)–Ni	112.2 (11)
	85.3 (5)		113.9 (7)
P–Ni–C(16)	178.4 (8)	H$_3$C(4)–As(1)–C(1)	106.7 (15)
		H$_3$C(9)–As(2)–C(6)	102.8 (15)
Ni–C(16)–N	176 (2)	H$_3$C(14)–As(3)–C(11)	99.0 (14)
Ni–As(1)–C(1)	121.4 (9)		102.8 (9)
Ni–As(2)–C(6)	122.2 (10)		
Ni–As(3)–C(11)	123.7 (9)	H$_3$C(5)–As(1)–C(1)	97.0 (12)
	122.4 (6)	H$_3$C(10)–As(2)–C(6)	97.4 (15)
		H$_3$C(15)–As(3)–C(11	100.4 (14)
As(1)–C(1)–C(2)	111 (2)		98.2 (8)
As(2)–C(6)–C(7)	107 (2)		
As(3)–C(11)– C(12)	110 (2)	H$_3$C(4)–As(1)–H$_3$C(5)	103.0 (14)
	109 (1)	H$_3$C(9)–As(2)– H$_3$C(10)	100.7 (13)
C(1)–C(2)–C(3)	108 (2)	H$_3$C(14)–As(3)– H$_3$C(15)	104.3 (16)
C(6)–C(7)–C(8)	109 (3)		102.7 (9)
C(11)–C(12)– C(13)	111 (2)		
	110 (1)	O(1)–Cl–O(2)	108.0 (22)
		O(1)–Cl–O(3)	113.2 (21)
C(2)–C(3)–P	117 (2)	O(1)–Cl–O(4)	110.7 (19)
C(7)–C(8)–P	115 (2)	O(2)–Cl–O(3)	110.1 (21)
C(12)–C(13)–P	112 (2)	O(2)–Cl–O(4)	108.2 (17)
	114 (1)	O(3)–Cl–O(4)	106.7 (17)
C(3)–P–Ni	117.8 (9)		109.5 (8)
C(8)–P–Ni	119.1 (10)		
C(13)–P–Ni	116.6 (9)		
	117.8 (6)		

[a] The standard deviations of the last significant figures are enclosed in parentheses.

specified atoms along with the perpendicular distances of these and other atoms from the planes were calculated with the Smith program.[19]

Discussion

The trigonal-bipyramidal configuration of the [Ni-(TAP)CN$^+$] cation is shown in Figure 1. Although no crystallographic symmetry is demanded by the space group (i.e., all atoms are in general positions), the framework of the idealized cation which consists of a central nickel atom surrounded by three arsenic atoms at equatorial sites and a phosphorus atom and a cyanide group in apical positions possesses C_{3v}–3m symmetry. The addition of the trimethylene chains which connect the phosphorus atom to each arsenic atom lowers the symmetry of the idealized cation to C_3-3. The ClO$_4^-$ anion exhibits, within the limits of experimental error, the expected tetrahedral configuration.

(19) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.
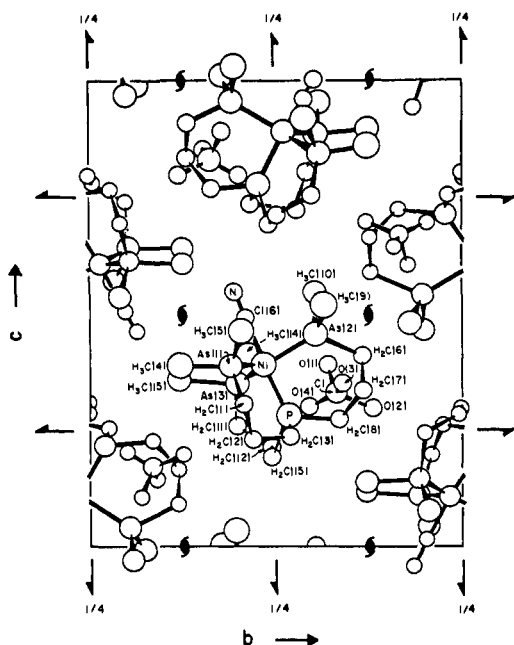
Figure 2. [100] projection of the orthorhombic unit cell of [Ni-(TAP)CN+]ClO₄⁻.

Figure 3. [010] projection of the orthorhombic unit cell of [Ni-(TAP)CN+]ClO₄⁻.

The [100] and [010] projections (Figures 2 and 3, respectively) show the orientations of the four formula units in the noncentrosymmetric unit cell. The closest approaches of oxygen atoms to methylene carbon atoms (3.25 A) and to methyl carbon atoms (3.72 A) indicate that any possible hydrogen bonding is negligible and that the ionic crystal is held together primarily by the usual electrostatic forces.

Nickel(II) has a d^8 electronic configuration; of the eleven five-coordinated metal complexes with a d^8 configuration for which solid-state structural data are available,[20,21] six are best described as trigonal-bipyramidal configurations and five as tetragonal-pyramidal configurations. Of these six trigonal-bipyramidal structures, only one, [Pt(QAS)I+][B(C₆H₅)₄⁻],[9] contains a multidentate ligand, and no detailed structural parameters have been published for this compound. Hence, this work presents the first detailed structural report on a multidentate trigonal-bipyramidal complex of a d^8 transition metal atom

The P–Ni–CN angle of 178.4° and the three As–Ni–As angles of 119.6, 120.3, and 118.1° differ only slightly from the respective values of 180 and 120° for a regular trigonal bipyramid. That the sum of three As–Ni–As angles is slightly less than 360° results from the fact that the nickel atom is displaced from the plane of the three equatorial arsenic atoms by 0.19 A toward the apical phosphorus atom. This is in contrast to [Pt-(QAs)I+] where the central platinum atom is reported to be displaced slightly toward the axial iodide ligand.[9]

The average Ni–As bond distance of 2.32 A is somewhat longer than that of 2.26 A in the distorted tetragonal-pyramidal complex Ni(TAS)Br₂, where TAS = methylbis(3-dimethylarsinopropyl)arsine.[22] The Ni–P bond length of 2.21 A is comparable to those of
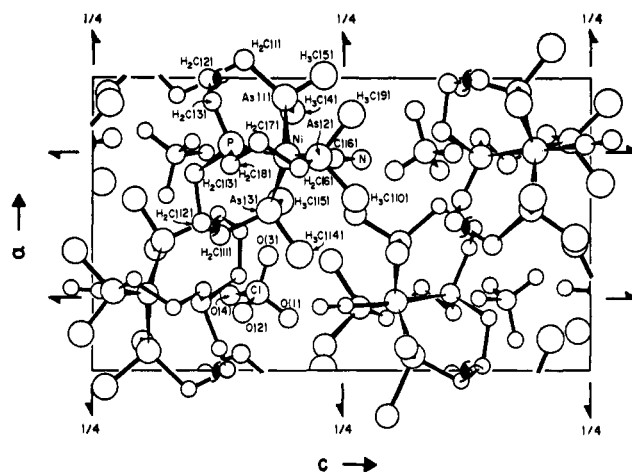
2.18 A in Ni[HP(C₆H₅)₂]₃Br₂[21] and 2.15 A in [(C₆H₅)₂-PNiC₅H₅]₂.[23] The average As–C distance of 1.98 A is comparable to the average As–C distance in {[(C₆H₅)₂-CH₃AsO₄]₄NiClO₄+} (1.93 A)[24] and in [HgBr₂(QAS)]-CH₂Cl₂(1.93 A).[25] The Ni–C and C–N bond lengths of 1.87 and 1.12 A, respectively, can be compared to the corresponding distances of 1.76 and 1.12 A in Ni(CN)₂-NH₃·C₆H₆[26] and of 1.86 and 1.15 A in Ni(CN)₂-NH₃·nH₂O,[27] but the high standard deviations which arise from the use of essentially two-dimensional data in the latter two complexes render the differences insignificant. The average P–C bond distance of 1.83 A is comparable to those in P(C₆H₅)₅ [1.850 (equatorial) and 1.987 A (apical)],[28] RhH(CO)[P(C₆H₅)₃]₃ (1.83 A),[29] and [(C₆H₅)₂PNiC₅H₅]₂ (1.84 A).[23]

The view of [Ni(TAP)CN+] down the idealized three-fold rotation axis (the drawing on the left of Figure 1) clearly shows that all three trimethylene chains pucker in the same direction. In order to differentiate between this conformation and its mirror image (i.e., the conformation in which all three trimethylene chains pucker in the opposite direction), the anomalous scattering method of Peerdeman, van Bommel, and Bijvoet[30,31] was used. Least-squares refinement of both possible conformers gave R_1 and R_2 values which were both lowered by 0.5% for the above conformer. This choice was corroborated by a comparison of the observed uncorrected film intensities for pairs of corresponding reflections (e.g., $I(hkl)$ and $I(hk\bar{l})$) for which the structure factor calculations showed the greatest difference in magnitude.

An examination of the nonbonding distances in the [Ni(TAP)CN+] cation indicates that the observed idealized trigonal-bipyramidal conformation of C_3 symmetry is the preferred one. The methylene hydrogen atoms of

(20) E. L. Muetterties and R. A. Schunn, Quart. Rev. (London), 20, 245 (1966), and references contained therein.
(21) J. A. Bertrand and D. L. Plymale, Inorg. Chem., 5, 879 (1966).
(22) G. A. Mair, H. M. Powell, and D. E. Henn, Proc. Chem. Soc., 415 (1960).

(23) J. M. Coleman and L. F. Dahl, J. Am. Chem. Soc., 89, 542 (1967).
(24) P. Pauling, G. B. Robertson, and G. A. Rodley, Nature, 207, 73 (1965).
(25) G. Dyer, D. C. Goodall, R. H. B. Mais, H. M. Powell, and L. M. Venanzi, J. Chem. Soc., Sect., A, 1110 (1966).
(26) J. H. Rayner and H. M. Powell, J. Chem. Soc., 319 (1952).
(27) J. H. Rayner and H. M. Powell, ibid., 3412 (1958).
(28) P. J. Wheatley, ibid., 2206 (1964).
(29) S. J. LaPlaca and J. A. Ibers, Acta Cryst., 18, 511 (1965).
(30) A. F. Peerdeman, A. J. van Bommel, and J. M. Bijvoet, Proc. Koninkl. Ned. Akad. Wetenschap., B54, 16 (1951).
(31) A lucid discussion of the determination of absolute configurations by anomalous scattering along with relevant references is found in M. J. Buerger, "Crystal-Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, pp 542–550.

the three carbon atoms bonded to the apical phosphorus atom are staggered in such a way that these methylene carbon atoms can approach within the observed value of 2.8 A of each other, much closer than the 4.0 A approach suggested by the van der Waals radius of the methylene group.[32] It should be noted that a diastereomeric form of [Ni(TAP)CN+] can theoretically occur in which two trimethylene chains pucker in one direction and a third trimethylene chain puckers in the opposite direction. Since this diastereomer would require one nonbonding C···C distance of only 2.2 A for two methylene carbon atoms attached to the apical phosphorus atom, its possible formation can be precluded by steric considerations as being energetically unfavorable unless there is considerable angular distortion.

The results obtained in this study indicate the need of further structural investigations of five-coordinate metal complexes of d^8 configuration. Insight into the causes of the displacement of the central metal atoms from the equatorial triarsenic planes in the [Ni(TAP)CN+] and the [Pt(QAS)I+] cations could be gained from the synthesis and X-ray structural analysis of the cyanide analog of [Pt(QAS)I+]. A probable rationale is that the observed distortion is a means of minimizing nonbonding atomic repulsions without unduly increasing the metal–ligand bond lengths (thus weakening the metal–ligand bonds). Although the appropriate sums of the van der Waals radii[32] of As (2.0 A), P (1.9 A), and C (1.5 A) suggest nonbonding As···As contacts of 4.0 A, As···P contacts of 3.9 A, and As···CN contacts of 3.5 A in [Ni(TAP)CN+], the observed average nonbonding distances are 4.0, 3.3, and 2.9 A, respectively. A regular trigonal-bipyramidal configuration with the observed Ni–As, Ni–P, and Ni–CN bond lengths would possess nonbonding As···P and As···CN contacts of 3.2 and 3.0 A, respectively. Hence, in order to minimize the nonbonding interactions, the arsenic atoms are displaced toward the cyanide group, increasing the As–Ni–P angles from 90° to the observed average value of 95°. In [Pt(QAS)I+] the monodentate iodide ligand has a larger van der Waals radius than the apical arsenic atom (2.15 vs. 2.0 A)[32] so that the distortion is in the opposite direction, effectively pulling the central platinum atom below the triarsenic plane. If the minimizing of nonbonding repulsions is the dominant factor in these observed distortions, the central platinum atom in [Pt(QAS)CN+] should likewise be displaced from the plane of the three equatorial arsenic atoms toward the apical arsenic atom.

An X-ray determination of the bromide analog of [Ni(TAP)CN+], which has also been synthesized by Benner, Hatfield, and Meek,[5] is being carried out in order to compare the structural features of the two cations. A comparison of Weissenberg photographs of [Ni(TAP)CN+]ClO4- and [Ni(TAP)Br+]ClO4- has indicated that their crystal structures are not isomorphous. On the basis of spectral observations, Meek[33] has suggested that the cation of the latter bromide compound is possibly distorted toward a tetragonal-pyramidal geometry. Detailed structural parameters of [Ni(TAP)Br+]ClO4- should provide significant information concerning the nature and extent of this molecular deformation.

(32) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp 260–261.

(33) D. W. Meek, private communication to L. F. Dahl, 1965.

Racemization and Proton Exchange in the trans,trans-Dinitrobis(N-methylethylenediamine)cobalt(III) Ion

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Abstract: The rates of proton exchange and racemization at the optically active nitrogen centers in the trans,trans-dinitrobis(N-methylethylenediamine)cobalt(III) ion have been measured. Substantial retention of configuration was observed in the proton exchange, $k_D/k_R \sim 90,000$. Rates and activation parameters are compared with previous results. Conformational effects and the significance of the substituents in the 1 and 6 positions of the octahedral ion are also discussed.

R ecently complexes of the form [Co(NH3)4sar]2+ [1] and [Co(NH3)4N-Meen]3+ [2] (sar = sarcosinate anion, N-Meen = N-methylethylenediamine) have been resolved into their catoptromers (mirror-image forms) where the sole source of asymmetry resides in the coordinated secondary amine N atom. This is achieved

(1) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, 88, 4630 (1966).

(2) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, 89, 825 (1967).