Ni(I) complex (ν_{CN} 2065 and 2100 cm^{-1}) followed by the slow formation of the final products, $[Ni(CN)_2(dpb)]_2$ (ν_{CN} 2115 cm^{-1}) and $Ni(CN)_2(dpb)_2$ (ν_{CN} 2100 cm^{-1}).[7] The formation of small amounts of the pentacoordinated species of Ni(II) which displays the ν_{CN} band at 2100 cm^{-1} does not complicate the assignment of the strong band at 2100 cm^{-1} to Ni(I) species, because the intensity of this band was very high, whereas the Ni(II) complex is sparingly soluble in benzene even in the presence of an excess of HCN. Moreover it is reasonable to suppose that both $[NiCN(dpb)_{1.5}]_2$ and $NiCN(dpb)_{1.5}\cdot HCN$ display a 2100-cm^{-1} ν_{CN} band, as experiments performed on some Ni(II) complexes, for example on $Ni(CN)_2(P(C_3H_7)_3)_2$,[9] show that quite similar adducts are formed and the ν_{CN} due to the CN coordinated directly to the metal is unaffected by the coordination of HCN.

The reaction between $Ni(dpb)_2$ and HCN was also followed in dichloroethane, and the ir pattern was similar to that observed in benzene, but the relatively good solubility of the pentacoordinated Ni(II) species complicated the assignment of the band at 2100 cm^{-1}.

Absorption spectra in the visible region were also taken during the reaction in dichloroethane and are consistent with the interpretation of the infrared spectrum. A few minutes after $Ni(dpb)_2$ had been added to an HCN solution at 20°, the visible spectrum (Figure 2) closely resembled that of a solution containing $[NiCN(dpb)_{1.5}]_2$ at the same initial concentration of $Ni(dpb)_2$ in the presence of the identical concentration of HCN. The final products were found to correspond to a mixture of $[Ni(CN)_2(dpb)]_2$ and the pentacoordinated species, which are known to exist in equilibrium.[7] Spectrophotometric determination of the total amount of Ni(II) complexes showed that 95% of the Ni(0) complex has been oxidized to Ni(II) species.

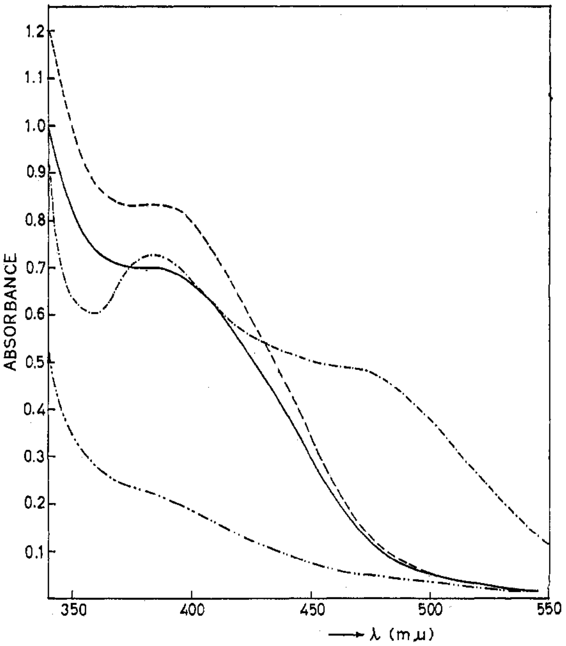

Figure 2.—Visible spectra of reaction solutions: ——, $[Ni(dpb)_2] = 4.8 \times 10^{-4}$ *M*, $[HCN] = 6.2 \times 10^{-2}$ *M*; -·-·-·-, t_∞; -··-··-, t_∞ after addition of dpb (*ca.* 1.2×10^{-2} *M*); ------, $[[NiCN(dpb)_{1.5}]_2] = 4.8 \times 10^{-4}$ *M*, $[HCN] = 6.2 \times 10^{-2}$ *M*. Cell path 0.5 cm.

The reactions of the Ni(I) complex $[Ni(CN)(dpb)_{1.5}]_2$ with HCN in $C_2H_4Cl_2$ and benzene were also investigated. The ir patterns in solution were found to be identical with those observed with $Ni(dpb)_2$, confirming thus that the Ni(I) complex is an intermediate in the oxidation of $Ni(dpb)_2$.

It would seem that the oxidative addition of HCN to $Ni(dpb)_2$ is rather peculiar in that no hydride species are discernible, no hydrogen is evolved, and two separated formal oxidation state changes of 1+ are observed. It may well be that very reactive hydrides such as $Ni(CN)(dpb)H$ or $Ni(dpb)_2H^+$ [3] are present in relatively low concentration.

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(9) B. Corain, to be submitted for publication.

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The Crystal Structure of Mercury(II) Cyanonitrate

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Infinite linear chains –M–CN–M–CN–M–, with disordered cyanide groups, occur in crystalline AuCN,[1] AgCN,[2] and $AgCN\cdot 2AgNO_3$;[3] chains of the type –Ag–NC–Hg–CN–Ag– occur in $Hg(CN)_2\cdot AgNO_3\cdot H_2O$.[4] The structure of $Hg(CN)(NO_3)$, reported here, was examined to see whether similar infinite linear chains –Hg–CN–Hg–CN–Hg– were present.

Experimental Section

Upon evaporation of a solution made up from a concentrated solution of $Hg(CN)_2$ and an equal volume of concentrated HNO_3, a mass of tetragonal and hexagonal prisms formed. The crystals were separated by hand under a microscope. A precession photograph of one of the tetragonal crystals was identical with a similar photograph from a known sample of $Hg(CN)_2$.

The infrared spectrum of the hexagonal crystals shows a C–N stretching band at 2245 cm^{-1}, indicative of a bridging cyanide group,[5] and characteristic nitrate bands. Only one report of the compound $Hg(CN)_2\cdot Hg(NO_3)_2$ mentions a hexagonal form. In 1839 Johnston[6] described the residue after evaporation of a dilute HNO_3 solution of $(HgCN)_2O$ as "quadrangular prisms, hexagonal plates, and pearly scales." He did not appear to realize that this was a mixture, not a pure compound.

The cell dimensions of the hexagonal crystals, estimated from film data, were determined accurately by least-squares calculations from the θ angle values of 17 peaks scanned with a diffractometer using Mo Kα radiation (λ 0.7107 Å). The dimensions are a = 5.422 (1) Å and c = 5.252 (2) Å. The density from flotation in thallous formate–thallous malonate solution, 3.60 (2) g/cm^3, agrees with the density of 3.585 (2) g/cm^3 calculated assuming one unit of $Hg(CN)(NO_3)$ per cell.

Precession and oscillation photographs showed no systematic extinctions and no doubling of the c dimension. The film data

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(1) *Nat. Bur. Stand. (U. S.), Circ.*, **No. 539**, **10**, 33 (1960); G. S. Zhdanov and A. E. Shugam, *Zh. Fiz. Khim.*, **19**, 519 (1945); G. S. Zhdanov and A. E. Shugam, *Acta Physicochim. U.R.S.S.*, **20**, 253 (1945).

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as well as the eventual counter data showed that the Laue group is $6/mmm$; therefore, the possible space groups are $P622$, $P6mm$, $P\bar{6}2m$, $P\bar{6}m2$, and $P6/mmm$. In all of these the Hg atom may be placed at 0, 0, 0. Two tests for pyroelectricity, the spoon test[7] and Kundt's test,[8] whereby a red lead oxide–sulfur mixture is blown onto heated crystals, were negative.[9]

The crystal used for intensity data collection was a regular hexagonal prism, approximately 0.7 mm long and 0.08 mm thick. It was mounted with c as the ϕ axis in a thin-walled glass capillary since the crystals decompose slowly in open air. Data were collected at room temperature with a four-circle Hilger and Watts automatic diffractometer, using Mo Kα radiation. The scan was in 120 2-sec steps of 0.01° in θ and ω from $-0.60°$ to $+0.60°$ with respect to the calculated setting. Background was counted for 120 sec at each limit of the scan. In all, 1468 intensities were collected from half the sphere of reflection out to $\theta = 37°$. Two standard reflection intensities, measured at intervals of 50 reflections, decreased by only about 1% from beginning to end, while the scatter was 1.5%; therefore, data scaling was deemed necessary.

Reflections were grouped with their equivalents (12 for hkl, 6 for $h0l$ and hhl). The intensity, I, and standard deviation, σ_I, were found from the peak intensities, P, and combined right and left backgrounds, B, according to

$$I = \left(\sum_1^n P - \sum_1^n B\right)\Big/ n$$

$$\sigma_I = \sqrt{\sum_1^n P + \sum_1^n B}\Big/ n$$

There were 171 nonequivalent reflections, all with intensities greater than σ_I, most over $3\sigma_I$. Intensities dropped off evenly with increasing Bragg angle because the Hg atom at the origin had 65% of the electrons.

The absorption coefficient, μ, is 293 cm^{-1}. Point-by-point absorption corrections and Lorentz–polarization corrections were made with a local modification of the program DATAP2.[10,11]

Structure Determination and Refinement

The light atoms were found, apparently in space group $P6/mmm$, on a Fourier map calculated with phases determined by the Hg atom only. Initially, $R = 0.229$ and $r = 0.132$.[12] After six cycles of least squares with isotropic light atoms and an anisotropic Hg atom, $R = 0.142$ and $r = 0.034$. Up to this point weights had been calculated according to

$$w = (T/(\sigma_I Lp))^2 = (1/\sigma_{|F_o|^2})^2$$

where T is the transmission factor and Lp the Lorentz–polarization factor. This weighting scheme gave too little weight to the weaker intensities; for the rest of the calculations the following weights were used: $w = 1$ for $F_o \leq 6.0$, $w = (6.0/F_o)^4$ for $F_o > 6.0$.[13] A graph of F_o *vs* F_c showed that the most intense reflections were affected by extinction; hence, the six with $F_c > 60$ were excluded.

Several more cycles of least squares improved the agreement to $R = 0.041$ and $r = 0.012$. After two final cycles with all atoms thermally anisotropic, $R = 0.0371$ and $r = 0.0097$. The solution in $P6/mmm$ requires that the nitrate groups are statistically distributed over the sites $^1/_3$, $^2/_3$, 0 and $^2/_3$, $^1/_3$, 0 as shown in the lower plane in the figure. Since the packing of the nitrates precludes this in any one plane, *i.e.*, any one plane is completely ordered, we interpret this to mean that successive planes are randomly distributed between the two orientations.[14] An alternative to be considered is that all of the nitrates are in one of these positions and that the space group symmetry is lowered to $P\bar{6}2m$ by the ordering. For comparison of the ordered nitrate model with the disordered model, the last two cycles were repeated with $P\bar{6}2m$ symmetry, giving the final agreement factors $R = 0.0379$ and $r = 0.0105$. The $\mathcal{R}$ factor ratio[15] here is 1.04 compared with $\mathcal{R}_{1,152,0.005} = 1.027$ so that we reject the hypothesis that $P\bar{6}2m$ is the correct space group. On a final difference map, no peak further than 1.0 Å from an atom position exceeded 0.6 e$^-$/Å^3. The final atomic coordinates and thermal parameters are listed in Table I.[16] The scattering factors including $\Delta f'$ and $\Delta f''$ for mercury were taken from ref 17.

TABLE I

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a]

Atom	x (y)	y (x)	z	B(isotropic), Å^2
Hg	0	0	0	2.81
O	0.533 (3)	0.067 (3)	0	4.8
N	$^2/_3$	$^1/_3$	0	3.1
CN(av)	0	0	0.393 (2)	3.6

Atom	$B(11)$, Å^2	$B(22)$, Å^2	$B(33)$, Å^2	$B(12)$, Å^2
Hg	3.14 (2)	3.14 (2)	2.17 (1)	3.14 (2)
O	3.0 (4)	2.1 (3)	9.3 (12)	2.1 (6)
N	3.1 (4)	3.1 (4)	2.8 (3)	3.1 (7)
CN(av)	4.0 (3)	4.0 (3)	2.9 (3)	4.0 (5)

[a] Standard deviation in the last digit is in parentheses. The form of the anisotropic temperature factor is: $\exp(-(B(11)h^2a^{*2}/4 + B(22)k^2b^{*2}/4 + B(33)l^2c^{*2}/4 + B(12)hka^*b^*/4))$.

Results and Discussion

The interatomic distances in mercury(II) cyanonitrate are Hg–CN(av) = 2.063 (9) Å, Hg–O = 2.727 (22) Å, C–N = 1.128 (13) Å, N–O = 1.251 (22) Å. Figure 1 is a perspective drawing of the structure with

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(7) C. W. Bunn, "Chemical Crystallography," 2nd ed, Oxford University Press, London, 1961, p 321.

(8) M. J. Buerger, "Elementary Crystallography," Wiley, New York, N. Y., 1956, p 188.

(9) Occasional crystals appeared to give a positive spoon test, but we believe this was an erroneous result. The crystals decompose on standing in the air to a product that contains an appreciable amount of water, as shown by the infrared spectrum. It is possible the erroneous results were due to slightly moist crystals.

(10) P. L. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).

(11) All computer calculations were made with the Control Data 6600 Computer of the University of Minnesota Computer Center. All Fourier and full-matrix least-squares calculations were made with the program UMLSTSQ by L. W. Finger. The calculations were actually made using monoclinic space groups with expanded structure factor and atom lists.

(12) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$. The numerator of r was the function minimized; the weight, w, is defined in the text.

(13) S. C. Abrahams and J. M. Reddy, *J. Chem. Phys.*, **43**, 2533 (1965). In the final refinement the standard deviation (in F^2) of an observation of unit weight was 2.73, showing that the relative weights used were fairly close to the correct weights.

(14) It is perhaps worth emphasizing that there are two independent kinds of disorder in this structure. The cyanide groups are disordered end for end, which would give rise to a zero-point entropy of $R \ln 2$. The nitrate layers are randomly in one of two orientations, which would give rise to a zero-point entropy of $R \ln 2^{N^{-(2/3)}} \cong 0$.

(15) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965). There is a certain ambiguity in the argument used here since we refine 13 parameters in either space group, and the argument might be made that we should use $\mathcal{R}_{13,152,\alpha}$ for comparison. However, the results quoted by Hamilton for absolute configuration determinations, where the same ambiguity arises, suggest that this is better regarded as a problem with one degree of freedom.

(16) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(17) International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A, p 202, and Table 3.3.2C, p 215.

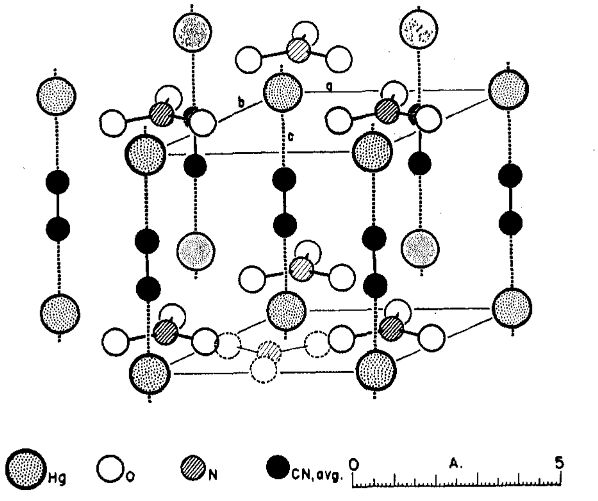

Figure 1.—The crystal structure of mercury(II) cyanonitrate.

nitrate occupying the same position in both layers. One nitrate group is dotted in on the alternate position.

The main feature of the structure is the infinite chains of sp hybridized Hg atoms linked by bridging CN groups paralleling the *c* axis, comparable to the structures of AuCN[1] and AgCN.[2] The apparent C–N bond length, 1.13 (1) Å, is within the range of normal C–N bond lengths, 1.13–1.20 Å.[18] The Hg–CN(av) distance, 2.06 (1) Å, may be compared with Hg–C distances to bridging cyanide of 2.04 (8) Å (av) in $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$[4] and 2.06 (3) Å in $Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$.[19] Reported Hg–N distances range from 2.05 to 2.09 Å,[20–24] but all involve sp^3, rather than sp, hybridized N atoms. In the basal plane the Hg atom interacts with six O atoms in three NO_3 groups. The geometry and Hg–O distance, 2.73 (2) Å, are not unusual.[4,25]

The anisotropic thermal parameters of the Hg and CN group atoms show that they are more constrained in the chain direction, as expected. The nitrate O atoms are vibrating strongly normal to the basal plane since their bonds are all in the plane. The abnormally large vibrations are presumably a consequence of the lack of any contacts between the O and other atoms in the *c* direction.

One final noteworthy feature of the structure of $Hg(CN)(NO_3)$ is the large amount of empty space in it. If closely packed, the atoms would occupy about 70% of the volume that they occupy here.

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(22) W. N. Lipscomb, *ibid.*, **4**, 266 (1951).
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Mössbauer Effect Study of Molecular Adducts of *trans*-Bis(triphenylphosphine)iridium Carbonyl Chloride

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As noted some time ago by Vaska,[1] the *trans*-bis(triphenylphosphine)iridium carbonyl chloride molecule, $IrCl(CO)((C_6H_5)_3P)_2$ (hereafter denoted Cl-VA), has the property of forming adducts with a number of small molecules such as H_2, O_2, Cl_2, etc. Further studies have indicated that variations in chemical or physical properties of the adducts may be interpreted as evidence for changes in the relative oxidation state of the central iridium atom.[2] Primarily on the basis of carbonyl stretching frequencies, the parent, planar compound Cl-VA has been assigned an oxidation state of 1+, 5d^8, while the most oxidized derivative, Cl-VA-Cl_2, has the 3+ valence, 5d^6. The iridium in other derivatives has been assigned intermediate, nonintegral valences. This classification is, of course, subject to several reservations, some of which are discussed by Vaska.[2] The Mössbauer effect (ME) in iridium isotopes offers another convenient probe of the electronic state of iridium, and in the following discussion we describe results of such an investigation employing the 73-keV level of iridium-193. The species chosen for study include those characteristic of the extreme cases of carbonyl stretching frequencies, together with certain intermediate species of particular interest such as the oxygenated and hydrogenated adducts.

The ground-state spin of iridium-193 is $^3/_2$, and the spin of the 73-keV level is $^1/_2$.[3] The parameters describing the Mössbauer data are the quadrupole splitting, $\Delta E = |(e^2qQ/2)\sqrt{1 + \eta^2/3}|$, and the isomer shift, δE. These data, with isomer shift referred to an iridium in osmium metal source, are given in Table I. Also given in Table I are the ν_{CO} frequencies of the adducts. As discussed below, it is convenient to plot isomer shift *vs.* ν_{CO}, and this is shown in Figure 1. The nuclear charge radius parameter $\delta R/R$ is taken as positive,[4,5] so increases in $|\psi(0)|^2$ correspond to more positive isomer shifts. We note that the signs of the efg's have not been explicitly determined in these experiments. Owing to admixtures of E2 and M1 radiation in the 73-keV transition, the quadrupole splitting pattern is perturbed by an axial magnetic field in an effectively symmetric fashion; *e.g.*, an experiment with Cl-VA-Cl_2 in an axial field of 65 kOe proved inconclusive with 0.5% statistics.[6] A minor complication is the source splitting of 0.052 cm/sec, which is due to the

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