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The Crystal and Molecular Structure of Diiodotetrakis(pyridine)nickel(II), [$Nipy_4I_2$]

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The crystal structure of diiodotetrakis(pyridine)nickel (II), [$Nipy_4I_2$] has been determined accurately by three-dimensional, single-crystal X-ray analysis. The orthorhombic cell of space group Pbcn has a = *9.678(4) Å,* b = *16.077(6) Å, and* c = *14.004(4) Å, with four molecules per unit cell (density = 1.88 g/cm^3 experimental, and 1.92 g/cm^3 calculated). The structural refinement was terminated at R = 0.042. The molecule was found to have the geometric* trans *configuration, and this supports electronic spectroscopic conclusions. The nickel atom is surrounded by the four nitrogen atoms of pyridine molecules so that the group (NiN_4) defines a plane. The four nitrogen atoms deviate but slightly from defininig a square. The I-Ni-I moiety is nearly linear so that any one Ni-I) vector deviates only slightly ($\sim$2) from being perpendicular to the (NiN_4) plane. The average Ni-N distance in [$Nipy_4I_2$] is the largest (2.127(7) Å) such bond length yet observed for high-spin Ni^{II}-pyridine complexes. Regarding the pyridine ring, the average C-C bond distances of coordinated pyridine are found to be shorter than those of the free pyridine molecule. It is also interesting that the two planes of each pair of* trans *pyridine molecules are found to be staggered ($\sim$90°), whereas both eclipsed and staggered configurations were previously reported for other, but somewhat related molecules. Each of the four pyridine molecules has a pitch angle of ca. 45° with respect to the near-C_4 axis along Ni-I. The pyridine molecules also define a four-blade propeller, since this "C_4" axis brings one pyridine molecule nearly into coincidence with the others. The structural relationships of [$Nipy_4I_2$] are also compared with those of other metal-pyridine complexes.*

Introduction

The prolific use of pyridine as an effective ligand resides in large part in three features, *i.e.*, it forms numerous reasonably stable complexes, its σ-electron as well as π-electron systems participate in bonding, and as a heterycyclic molecule it resembles to some extent pyrimidine and similar species having biological significance. Detailed and definitive X-ray structural information about pyridine-metal complexes is available only for [$Fepy_6$]$^{2+}$ in [$Fepy_6$][$Fe_4(CO)_{13}$],[1] the adducts [$Ni(S_2P(C_6H_5)_2)_2$] · 2py,[2] and [$Ni(S_2P(OC_6H_5)_2)_2$] · 2py,[3] and trans-bis(2,4-pentanedionato)-dipyridinenickel(II)[4] and its cobalt(II) analog[5]. The x-ray structures of two complexes of substituted pyridine molecules (3,5-dimethylpyridine, or 3,5-dpy; and 3,4-dimethylpyridine, or 3,4-dpy) have also been well determined recently, *viz.*, *trans*-[Ni(3,5-dpy)$_4$-(ClO_4)$_2$] [6] and *trans*-[Ni(3,4-dpy)$_4$](ClO_4)$_2$ [7]. There exist preliminary x-ray data[8-10] on *trans*-[$Nipy_4X_2$] (X^- = Cl^- or Br^-), *trans*-[$Mpy_4(NCS)_2$] (M^{II} = Co^{II} or Ni^{II}), and *trans*-[$Copy_4X_2$] (X^- = Cl^- or Br^-). However, these determinations[8-10] contain several weak features as a consequence of the nature x-ray structural computations of these structures, and as a consequence of assumptions entering the computations. In view of these facts, and because accurate structural data relate to recent extensive infrared, magnetic susceptibility, NMR contact shift, electronic absorption and magnetic circular dichroism studies[11-12], it was considered important to undertake the detailed analysis of one of these tetragonal systems, [$Nipy_4I_2$], which from spectroscopy is thought to have the *trans* geometry.

Results and Discussion

Bond distances and bond angles of [$Nipy_4I_2$] are given in Tables I and II, respectively, and the numbering system for atoms is shown in Fig. 1 which is also a stereoprojecton of the molecule. Other computational parameters appear in Table III, and hydrogen positions in Table IV. The atomic positions

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[1] R.L. Doedens and L.F. Dahl, *J. Amer. Chem. Soc.*, *88*, 4847 (1966).

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[10] M.A. Porai-Koshits and A.S. Antsyshkina, *Kristallografiia*, *3*, 676 (1958).

[11] S.M. Nelson, Chapter 5 in « Transition Metals-Part 1 » vol. 5, D.W. A. Sharp, ed., of Inorganic Chemistry Series One, Butterworth (1972), and references therein. For example: R.E. Cramer and R.S. Drago J. Amer. Chem. Soc., *92*, 66 (1970); D. Forster, Inorg. Chim. Acta, 5, 465 (1971); R.H. Holm, G.W. Holm, G..W Everett, and W.D. Horrocks, J. Amer. Chem. Soc., *88*, 1071 (1966); D.A. Rowley and R.S. Drago, Inorg. Chem., 6, 1092 (1967); R.H. Nuttal, A.F. Cameron and D.W. Taylor, J. Chem. Soc. (A), 3103 (1971); and A.B.P. Lever, « Inorganic Electronic Spectroscopy », Elsevier, New York (1968).

[12] A.F. Schreiner and D.J. Hamm, *Inorg. Chem.*, *12*, 2037 (1973).

Table I. Bond Lengths (Å) in $[\mathrm{Nipy_4I_2}]$.

Ni(1)-I(2)	2.886(1)
Ni(1)-N(3)	2.114(8)
Ni(1)-N(7)	2.130(8)
Ni(1)-N(11)	2.125(6)
N(3)-C(4)	1.342(8)
C(4)-C(5)	1.373(10)
C(5)-C(6)	1.381(10)
N(7)-C(8)	1.332(8)
C(8)-C(9)	1.405(10)
C(9)-C(10)	1.362(9)
N(11)-C(12)	1.369(10)
C(12)-C(13)	1.372(11)
C(13)-C(14)	1.351(12)
C(14)-C(15)	1.359(12)
C(15)-C(16)	1.401(11)
C(16)-N(11)	1.338(9)

Table II. Bond Angles (Deg) in $[\mathrm{Nipy_4I_2}]$.

I(2)-Ni(1)-N(3)	87.6(0)
I(2)-Ni(1)-N(7)	92.4(0)
I(2)-Ni(1)-N(11)	89.2(2)
N(3)-Ni(1)-N(11)	93.5(2)
N(7)-Ni(1)-N(11)	86.5(2)
Ni(1)-N(3)-C(4)	120.9(4)
Ni(1)-N(7)-C(8)	120.3(4)
Ni(1)-N(11)-C(12)	122.1(5)
N(3)-C(4)-C(5)	122.1(7)
C(4)-C(5)-C(6)	120.0(8)
N(7)-C(8)-C(9)	121.5(7)
C(8)-C(9)-C(10)	118.9(7)
N(11)-C(12)-C(13)	122.5(7)
C(12)-C(13)-C(14)	120.0(8)
C(13)-C(14)-C(15)	118.9(8)
C(14)-C(15)-C(16)	119.8(7)
C(15)-C(16)-N(11)	121.9(7)
C(16)-N(11)-C(12)	116.8(8)
C(5)-C(6)-C(5')	117.6(8)
C(9)-C(10)-C(9')	119.7(8)
C(15)-C(14)-C(13)	118.9(8)

not numbered are simply related to the ones which bear numbers through the genuine C_2 axis, *viz.*, C_2-[N(3) — Ni — N(7)]. The first feature immediately evident from these data is that the molecule has the *trans* geometry, or *trans*-$[\mathrm{Nipy_4I_2}]$, with the I — Ni — I group nearly linear. This confirms the same conclusion drawn from 80°K electronic spectra of $[\mathrm{Nipy_4I_2}]$ reported by other research groups.[12,13] The Ni — I bond distance is 2.886(1) Å, which is 0.034 Å shorter than the sum of ionic radii of 2.92 Å.[14] This is similar to the 0.042 Å value for t-$[\mathrm{Nipy_4Cl_2}]$. It is also of some interest to note that Ni — I bond directions are not precisely perpendicular to the plane of $(\mathrm{NiN_4})$. Thus, the Ni — I(2) vector "leans away" from N(7) because angle I(2) — Ni — N(7) is 92.4(0)°.

The average Ni — N (Ni — py) distance of $[\mathrm{Nipy_4I_2}]$ is 2.127(7) Å, which is the largest such bond length yet reported. It is further interesting to compare this bond length with other octahedral molecules containing the $\mathrm{Ni^{II}}$—pyridine moiety (see Table V). In *trans*-$[\mathrm{Nipy_4Cl_2}]$ for example, the Ni–N bond length is reported[8] to be only 2.00(5) Å, which makes this the shortest such bond length in a high-spin, six-coordinated, $\mathrm{Ni^{II}}$-pyridine complex. The $\mathrm{I^-}$ being larger than $\mathrm{Cl^-}$ is perhaps responsible for producing a somewhat expanded $(\mathrm{Nipy_4})$ sub-coordination sphere. It can also be seen in Table V that, within experimental uncertainties, the Ni–N distance in $[\mathrm{Nien_3}](\mathrm{NO_3})_2$ containing the saturated amine is that of the Ni — N distances of Ni — py compounds. The larger distance of the N,N-dimethylethylenediamine, on the other hand, is probably the result of intramolecular crowding. Furthermore, the adduct type of pyridine molecules are crystallographically not different from the other coordinated pyridine molecules on the basis of $\mathrm{Ni^{II}}$-N bond distances.

The five-atom group $(\mathrm{NiN_4})$ is exactly planar as a consequence of the space group. However, the four nitrogen atoms do not exactly define the corners of a perfect square (Fig. 2), since the atoms N(11) — Ni — N(11′) do not precisely fall on a straight line, or angle N(7) — Ni — N(11) is 86.5(2)°.

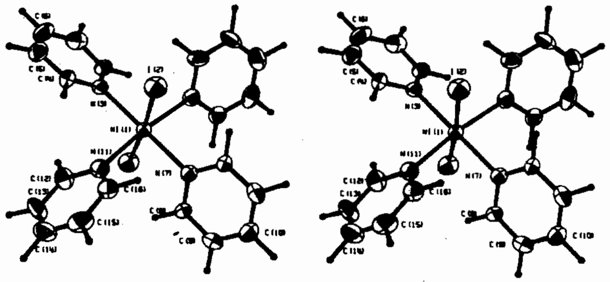

Figure 1. A stereodrawing of *trans*-$[\mathrm{Ni(pyridine)_4I_2}]$ and atom labels for Table I-IV.

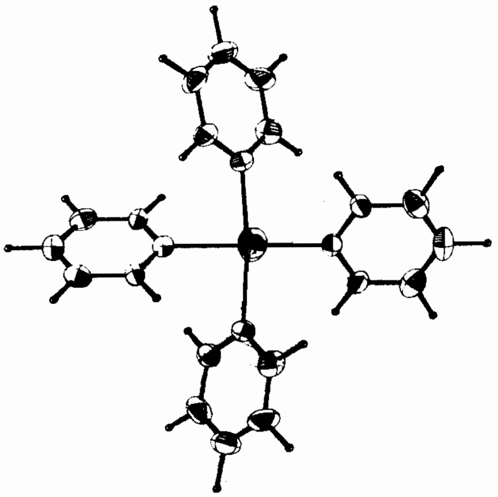

Figure 2. Structural view of t-$[\mathrm{Nipy_4I_2}]$ perpendicular to the $\mathrm{Ni(N_4)}$ plane and along the I—Ni—I axis.

On focusing one's attention on the pyridine molecules, it is to be noted first that each of them within $[\mathrm{Nipy_4I_2}]$ is planar. Secondly, the C_2 axes within the pyridine molecule containing N(3), or pyridine — N(3), and pyridine — N(7) are colinear,

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(13) S.M. Nelson and T.M. Shepherd, *J. Chem. Soc.*,3276 (1965).

(14) L. Pauling, «The Nature of the Chemical Bond», 3rd ed., Cornell University Press, Ithaca, New York (1960).

Table III. Final Positional Parameters, Thermal Vibration Parameters, and Their Standard Deviations, of Atoms Other than Hydrogen. (The values have been multiplied by 10^4. The temperature factor is in the form: $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}\ell^2+b_{12}hk+b_{13}h\ell+b_{23}k\ell)]$.)

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni(1)	5000(0)	4043(1)	7500(0)	58(2)	18(1)	30(1)	0(0)	10(1)	0(0)
I(2)	2981(1)	4117(0)	5985(0)	93(1)	37(0)	46(0)	1(1)	—26(1)	3(1)
N(3)	5000(0)	5359(4)	7500(0)	51(10)	20(3)	40(5)	0(0)	—3(13)	0(0)
C(4)	5230(7)	5787(4)	6692(5)	80(10)	21(3)	39(4)	—5(9)	6(11)	10(6)
C(5)	5254(8)	6641(4)	6675(6)	90(11)	34(4)	52(5)	—4(11)	—25(13)	23(8)
C(6)	5000(0)	7086(6)	7500(0)	113(17)	20(5)	68(9)	0(0)	—38(22)	0(0)
N(7)	5000(0)	2718(4)	7500(0)	71(11)	23(3)	34(5)	0(0)	11(13)	0(0)
C(8)	6171(7)	2300(4)	7634(5)	73(9)	18(3)	46(5)	4(9)	24(12)	—4(7)
C(9)	6199(8)	1426(4)	7644(6)	67(10)	37(4)	59(6)	19(11)	28(13)	—1(8)
C(10)	5000(0)	1001(6)	7500(0)	132(19)	23(5)	75(9)	0(0)	75(23)	0(0)
N(11)	6585(6)	3963(3)	6455(4)	86(8)	27(3)	29(3)	0(8)	15(9)	—5(5)
C(12)	7800(7)	4394(4)	6535(5)	79(11)	36(3)	43(4)	—30(10)	—14(12)	—9(7)
C(13)	8898(8)	4264(5)	5934(6)	55(10)	51(5)	65(6)	—20(11)	32(14)	—3(9)
C(14)	8815(9)	3681(5)	5241(5)	101(12)	46(4)	49(5)	29(12)	47(15)	—1(9)
C(15)	7615(9)	3254(4)	5130(5)	155(13)	33(4)	36(4)	30(12)	17(15)	—22(7)
C(16)	6500(7)	3411(4)	5742(5)	94(11)	29(3)	33(4)	—4(10)	8(11)	—13(6)

Table IV. Hydrogen Atom Parameters. (The values for the coordinates has been multiplied by 10^3. The values for the isotropic temperature factors have been multiplied by 10^1.)

	AT	X	Y	Z	B
H(17)	C(4)	539	543	603	38
H(18)	C(5)	549	697	599	38
H(19)	C(8)	712	265	774	38
H(20)	C(9)	717	110	777	38
H(21)	C(12)	789	487	712	38
H(22)	C(13)	984	464	599	38
H(23)	C(14)	970	354	476	38
H(24)	C(15)	751	277	456	38
H(25)	C(16)	551	306	563	38
H(26)	C(6)	500	776	750	38
H(27)	C(10)	500	30	750	38

Table V. Nickel(II)—Nitrogen Distances in Several Molecules.

	Ni-N(Å)	Reference
$[Nipy_4Cl_2]$	2.00(5)	8
$[Ni(S_2P(C_6H_5)_2)_2]$: 2py	2.083(13)	2
$[Ni(3,5\text{-}dpy)_4(ClO_4)_2]$	2.093(2)	6
$[Ni(S_2P(OC_6H_5)_2)_2]\cdot 2py$	2.11(1)	3
$[Ni(acac)_2]$: 2py	2.112(5)	4
$[Nien_3](NO_3)_2$	2.120(13)	16
$[Nipy_4I_2]$	2.127(7)	This work
$[Ni(AA)_2(NO_2)_2]$*	2.219(12)	17

* AA is N,N-dimethylethylenediamine.

but the C_2 axes within pyridine — N(11) and pyridine-N(11′) do not quite coincide, so that these two C_2 axes intersect. (Figs. 1 and 2).

It is of further interest that carbon-carbon bond distances within the coordinated pyridine molecules in $[Nipy_4I_2]$ appear to be contracted compared to those of the noncoordinated molecule. In this study one finds average distances of C_2-N = 1.345 Å, C_2-C_3 = 1.391 Å, and C_3-C_4 = 1.398 Å.[15] Sub-pyridine molecules the distances are C_2-N = 1.342 Å, C_2-C_3 = 1.391 Å, and C_3-C_4 = 1.398 Å.[15] Subscripts refer to the positions in a pyridine ring with nitrogen being "N_1". A similar pyridine coordination-contraction was observed by Elder[4] for the adduct $Ni(acac)_2$ 2py, with C_2-N = 1.332 Å, C_2-C_3 = 1.380 Å, and C_3-C_4 = Å. Even shorter distances appear in the cobalt analog, $[Co(acac)_2]$:2py.[5] However, the presence of reasonably large carbon thermal motions of our $[Nipy_4I_2]$ may shed some doubt on the true significance of these bond contractions.

The relative orientations of the planes of coordinated pyridine molecules is an interesting feature for *trans*-$[Nipy_4I_2]$ studied here and the comparison with several other complexes. Elder[4] found in 1968 that the pair of *trans* pyridine molecules in $[Ni(acac)_2]$. · 2py were eclipsed (the two *trans* pyridine molecules are in the same plane), whereas earlier that same year[5] he determined that the two pyridine molecules in the cobalt(II) analog, $[Co(acac)_2]\cdot 2py$, were staggered (the two planes of the pyridine molecules were perpendicular). Another eclipsed case is $[Ni(S_2P(C_6H_6)_2)_2]$ 2py as discovered by Porta, Sgamellotti, and Vinciguerra,[2] and the same eclipsing is present in an adduct of a dithiophosphate complex, $[Ni(S_2P(OC_6H_5)_2)_2]\cdot 2py$, studied by Ooi and Fernando,[3] and also in $[Fepy_5]^{2+}$.[1] The cases with staggered *trans* pyridine molecules are $[Nipy_4Cl_2]$,[8] and the 3,5-dimethylpyridine (3,5-dpy) complex trans-$[Ni(3,5\text{-}dpy)_4)(ClO_4)_2]$,[6] but in the first of these two complexes the stagger angle is uncertain, but it is well known in the second compound. This relatively large uncertainty (70° — 90°) also exists for *trans* pyridine molecules in $[Nipy_4Br_2]$[9] and $[Nipy_4(NCS)_2]$[10] Thus, we report for $[Nip_4I_2]$· the most accurately determined stagger angle for any unsubstituted tetrapyridine complex, *viz.*, 88.3° and 90° for each pair of pyridine molecules. An "end-on" view of one of the two pairs of pyridine molecules is shown in Fig. 3, in which the 90° relationship is obvious.

It is also found that the four pyridine molecules together are arranged in propeller, or paddlewheel, fashion, each pyridine molecule having approximately the same pitch angle relative to the line going through I(2) — Ni — I(2′). Madaule-Aubry and Brown[6] found a very similar situation in the 3,5-

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(15) B. Bak, L. Hansen and J. Rastrup-Anderson, *J. Chem. Phys.*, 22, 2013 (1954).

dimethylpyridine complex, [$Ni(3,5\text{-}dpy)_4(ClO_4)_2$]. Very interesting, however, is the case[7] of [$Ni(3,4\text{-}dpy)_4](ClO_4)_2$, in which the planes of the four pyridine molecules are co-directional with the C_4 axis of (NiN_4).

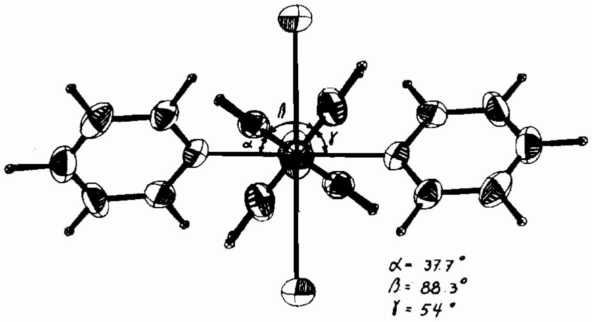

Figure 3. Structural view with t-[$Nipy_4I_2$] being viewed parallel to the $Ni(N_4)$ plane, and with an end-on look at two staggered pyridine molecules in *trans* position (i.e., those two lying on the crystallographic C_2 axis).

Returning to Fig. 3 of [$Nipy_4I_2$] and the possible orientations of pyridine molecules, we point out first that their four planes could not lie in the plane of (NiN_4) since the distances of approach of hydrogen atoms from adjacent pyridine molecules would be to small. Regarding the other extreme orientation, the hydrogen, iodide interactions would be too large if the pyridine molecules took up positions perpendicular to the plane of (NiN_4), or co-directional with the near-C_4 axis of (NiN_4) (Fig. 4). Thus it appears that the experimentally found pyridine orientations are intermediate between each of these extremes.

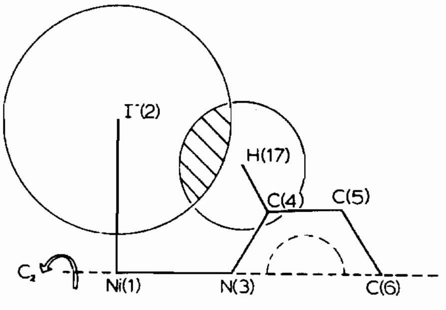

Figure 4. The interaction between coordinated I^- and H (attached to py) with the hypothetical orientation of the pyridine plane perpendicular to the (NiN_4) plane, or co-directional with I—Ni. The ionic radius of I^- and van der Waal radius of H were used here.

Elder's packing energy calculation[4] rules out the pπ(py) — dπ(Ni) interaction as being very important, but such an effect may be responsible for the small rotation (~9°) of the 88.3° — staggered pyridine pair (see Fig. 3) so as to prevent the occurence of a precisely symmetrical pitch with respect to the plane of (NiN_4). Intermolecular interactions could also produce small deviations, however.

Finally, it is pointed out that the previously reported assumption[8-10] that each of the pyridine molecules is skewed an equal angle of 45° to the plane of (NiN_4) is not correct, *viz.*, the angles are larger than 45° for one pyridine plane but smaller for another pyridine plane *trans* to the first, and this is obvious from Fig. 3.

Experimental Section

Compound Preparation and Crystal Growth. Diiododotetrakis(pyridine)nickel(II), [$Nipy_4I_2$], was prepared (according to the method of Nelson and Shepherd[13] by carefully adding a hot ethanolic solution of pyridine (~4.5 mole) dropwise to a hot ethanolic solution of NiI_2 (1.0 mole) which had been freshly prepared (according to Goodgame and Venanzi[18]. The dark gree solution was allowed to cool slowly to room temperature during wich time crystals suitable for x-ray analysis were formed. The analysisi of crystals, from which we chose the one for the present study, was as follows (%): Ni 9.27 (calc 9.34), C 38.29 (calc 38.18), N 9.11 (calc 8.94), and H 3.22 (calc 3.32). During the duration of the x-ray analysis the crystal was kept enclosed in a capillary.

X-Ray Analysis of [$Nipy_4I_2$]. A large crystal of [$Nipy_4I_2$] was cut to a suitable size (0.4 mm × 0.3 mm × 0.3 mm) and surveyed on a precession camera Both the survey and data collection were performed at ambient room temperature. The crystal system was found to be orthorhombic, space group Pbcn; Z = 4. Cell dimension were a = 9.678(4), b = 16.077(6), c = 14.004(4). The calculated density was 1.92 g/cm³ (density observed by flotation in a mixture of CCl_4 and 1,1,2,2-tetrabromoethane, 1.88 gcm³). The total number of reflections was 1436 of which 1181 were non-zero A 1-Å data set (maximum 2θ = 42.0°) was collected on a Syntex P1 diffractometer using molybdenum radiation wich had been monochromated by a graphite monochromator. A θ—2θ scan technique was employed, the scan rate was 2°/min, and the background was counted for half the scan time at each end of the scan. A single check reflection was monitored every 30 reflections; this reflection indicated no crystal damage and was reproducible well within counting statistics.

The diffractometer output was processed using subprograms of the CRYM crystallographic computer system[19]. The processing included corrections for background and for Lorentz and polarization effects. The effect of the graphite monochromator was included in these corrections. No correction for absorption was made. The data processing also included calculation of the F^2 value and its standard deviation for each reflection (reflections with observed intensities less than or equal to zero were assigned a value of zero intensity). The standard deviations were assigned on the basis of the following equation

$$\sigma^2(I) = S+(B_1+B_2)\sigma^2+(dS)^2$$

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(16) L.N. Swink and M. Atoji, *Acta Cryst.*, *13*, 639 (1960).
(17) M.G.B. Drew, D.M.L. Goodgame, M.A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, 363 (1964)
(18) D.M.L. Goodgame and L.M. Venanzi, *J. Chem. Soc.*, 616 (1963).
(19) D.J. Duchamp, Annual Meeting of the American Association of Crystallographers, Bozeman, Mont., 1964, Abstracts, paper B-14, p. 29.

where S is the scan count, B_1 and B_2 are the background counts, d is an empirical constant equal to 0.02 and $\alpha = n/2mt$ where n = scan range, m = scanning speed, and t = time for background count in seconds. Finally, the data set was placed on an absolute scale by means of Wilson statistics[20].

Determination of Structure and Refinement. The positions of the iodine ions in the unit cell were obtained from a three-dimensional Patterson map. A trial structure was obtained using conventional Patterson and Fourier techniques. This trial structure refined smoothly to an acceptable R index (R = 0.042). The refinement procedure included a full matrix least-squares treatment of coordinates, anisotropic temperature factors, and scale factor. Hydrogen positions were calculated and added to the structure factor calculation on the latter stages of refinement. Hydrogen parameters were not refined. The quantity minimized by the least-squares procedure is $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. A final difference Fourier revealed no missing or misplaced atoms.

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(20) A.J.C. Wilson, *Nature, 150,* 152 (1942).