exist in different electronic spin states. Hoskins and Kelly studied $Fe[S_2CN(C_4H_9)_2]_3$[13] and $Fe[S_2COC_2H_5]_3$[14] which, while exhibiting spin-state equilibria to a small extent, represent very nearly the high-spin ($S = {}^5/_2$) and low-spin ($S = {}^1/_2$) extremes, respectively. The Fe–S bond length in the former complex was found to be approximately 0.1 Å longer than that found in the latter, indicating significant Fe–S antibonding character for the $S = {}^5/_2$ electronic state. The fact that good single crystals of the present complex are obtained with 50% $S = 1$ spin state populated at the temperature of the X-ray measurements suggests that the $S = 1$ state has minimal antibonding character. Furthermore, the sulfur atom thermal ellipsoids are normal, except that the ellipsoid of the dtc sulfur atom, S(3), trans to the tfd ligand is elongated along the Fe–S bond axis (see Figure 2). This may or may not be indicative of some spin-state influence on this Fe–S bond length.

**Acknowledgment.**—We thank Drs. R. H. Holm and L. H. Pignolet of MIT for helpful discussions and for communication of their results prior to publication and Dr. G. N. Schrauzer for helpful comments regarding the description of the electronic structure. We are indebted to Dr. D. K. Smith of PSU and Dr. G. K. Smith of the Lawrence Radiation Laboratory, Livermore, Calif., for enabling us to obtain the stereoscopic ORTEP drawing. We thank the College of Science of PSU for an allocation of funds for computer time which made this study possible.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

# The Crystal and Molecular Structure of Hydridonitrosyltris(triphenylphosphine)iridium(I) Perchlorate, $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$

BY D. M. P. MINGOS AND JAMES A. IBERS*

*Received September 14, 1970*

The structure of hydridonitrosyltris(triphenylphosphine)iridium(I) perchlorate, $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group $Pbc2_1$ of the orthorhombic system with four molecules in a unit cell of dimensions $a = 11.335$ (9), $b = 21.992$ (17), and $c = 19.170$ (15) Å. The observed and calculated densities are 1.53 (±0.02) and 1.54 g $cm^{-3}$, respectively. Least-squares refinement has led to a final value of the conventional $R$ factor (on $F$) of 0.047 for the 1342 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well-separated monomeric ions and the geometry around the metal is described as distorted trigonal bipyramidal with the hydrido and nitrosyl ligands occupying the axial positions and the triphenylphosphine ligands the equatorial positions. The iridium atom lies 0.51 Å above the plane of the three phosphorus atoms. The hydrogen atom was not located in the structural determination. However its position has been inferred because the geometry of the other ligands around the metal is very similar to that found for the complexes $RhH(CO)(P(C_6H_5)_3)_3$ and $CoH(N_2)(P(C_6H_5)_3)_3$ for which the hydrogen atoms have been located. The iridium–nitrogen–oxygen bond angle of 175 (3)° suggests that this complex is best formulated as an $NO^+$ complex of iridium(I). Other important bond lengths in the molecule are as follows (Å): Ir–P, 2.346 (9), 2.341 (8), 2.334 (8); Ir–N, 1.68 (3); N–O, 1.21 (3). The bonding of the nitrosyl group in this complex is compared with that found in other iridium complexes, which have the nitrosyl ligand coordinated as $NO^-$. Also the geometries of the five-coordinate complexes $MH(X)(P(C_6H_5)_3)_3$ ($M = Co, X = N_2$; $M = Rh, X = CO$; $M = Ir, X = NO^+$) seem to be influenced by the degree of double bonding of the M–X bond, and it is proposed that electron-pair repulsions are responsible for the distortions from the ideal trigonal-bipyramidal geometry.

## Introduction

Interest has been shown recently in the ability of nitric oxide to bond to transition metals in two quite distinct ways. The complexes which have the nitrosyl ligand coordinated in a linear fashion have been formulated as complexes of $NO^+$ because of their close similarity to carbonyl complexes. In contrast the complexes which have a metal–nitrogen–oxygen bond angle of approximately 120° have been formulated as complexes of $NO^-$, which is isoelectronic with $O_2$. A possible reason that $NO^-$ and $O_2$ coordinate in a different fashion in certain iridium and rhodium complexes has been discussed previously.[1] It also appears that coordination of nitric oxide as NO is possible in certain paramagnetic complexes. However no structural evidence for this mode of coordination exists at present. We have shown that the iridium complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl, I)[2-4] and $IrXY(NO)(P(C_6H_5)_3)_2$ (X = Y = Cl;[1] X = I, Y = $CH_3$[5]) have the nitrosyl ligand coordinated as $NO^-$. The complex $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$, which was prepared by Reed and Roper[6] from perchloric acid and $Ir(NO)(P(C_6H_5)_3)_3$, is closely related to the iridium complexes mentioned above and it was of interest to examine the mode of coordination of the nitrosyl ligand in this complex. The low electronegativity and minimal steric requirements of the hydrido ligand could have an unusual effect on the metal–nitrosyl geometry.

---

(1) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

(2) D. J. Hodgson and J. A. Ibers, *ibid.*, **7**, 2345 (1968).

(3) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

(4) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 1282 (1969).

(5) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, **10**, 1043 (1971).

(6) C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$[a] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ir | 0.18978 (12)[b] | 0.15522 (5) | 1/4 | 0.00589 (10) | 0.00140 (2) | 0.00197 (4) | 0.00040 (8) | 0.00037 (18) | −0.00009 (10) |
| P1 | 0.0749 (9) | 0.2275 (4) | 0.1910 (5) | 0.0086 (11) | 0.0014 (3) | 0.0018 (3) | 0.0005 (4) | 0.0006 (6) | −0.0000 (2) |
| P2 | 0.1304 (8) | 0.0533 (4) | 0.2465 (10) | 0.0068 (8) | 0.0017 (2) | 0.0021 (3) | −0.0001 (3) | −0.0017 (10) | 0.0004 (5) |
| P3 | 0.3944 (7) | 0.1624 (4) | 0.2390 (8) | 0.0043 (7) | 0.0017 (2) | 0.0020 (6) | 0.0001 (4) | −0.0009 (5) | 0.0002 (3) |
| Cl | 0.3384 (9) | 0.3463 (6) | 0.4385 (5) | 0.0141 (15) | 0.0038 (3) | 0.0041 (4) | −0.0007 (8) | −0.0005 (6) | 0.0006 (4) |
| N | 0.1677 (25) | 0.1682 (14) | 0.3353 (17) | 0.0070 (35) | 0.0038 (11) | 0.0032 (12) | 0.0012 (16) | 0.0030 (17) | −0.0007 (10) |
| O1 | 0.1426 (27) | 0.1771 (14) | 0.3958 (16) | 0.0199 (48) | 0.0047 (11) | 0.0044 (12) | −0.0003 (16) | 0.0008 (20) | −0.0007 (10) |

| Group | $x_c$ | $y_c$ | $z_c$ | $\delta$ | $\epsilon$ | $\eta$ |
|---|---|---|---|---|---|---|
| R1 | 0.2041 (12) | 0.3264 (7) | 0.0974 (8) | 0.568 (17) | −2.620 (14) | −0.793 (15) |
| R2 | −0.0764 (12) | 0.3045 (5) | 0.3013 (8) | −1.391 (15) | −2.593 (13) | 2.269 (14) |
| R3 | −0.1221 (12) | 0.1845 (6) | 0.0818 (7) | −0.285 (15) | 2.506 (13) | −2.259 (16) |
| R4 | −0.1251 (12) | 0.0296 (6) | 0.3148 (6) | 0.079 (14) | −2.945 (13) | 2.660 (12) |
| R5 | 0.2901 (13) | −0.0188 (6) | 0.3587 (8) | 1.188 (18) | −2.348 (13) | 1.784 (19) |
| R6 | 0.1331 (10) | −0.0235 (8) | 0.1019 (8) | 0.166 (16) | 2.611 (16) | −1.663 (16) |
| R7 | 0.5216 (14) | 0.1555 (8) | 0.3906 (9) | −0.467 (16) | 2.991 (17) | −2.051 (15) |
| R8 | 0.5003 (12) | 0.2862 (7) | 0.1793 (7) | 0.855 (17) | −2.509 (13) | 2.707 (16) |
| R9 | 0.5103 (14) | 0.0536 (6) | 0.1519 (8) | 1.292 (19) | 2.336 (14) | 0.865 (19) |
| $ClO_4$ | 0.3388 (20) | 0.3410 (9) | 0.4388 (12) | 2.024 (19) | −3.049 (18) | −0.807 (18) |

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The numbers given here and in other tables are estimated standard deviations in the least significant figures. [c] $x_c$, $y_c$, and $z_c$ are the fractional coordinates of the group center; $\delta$, $\epsilon$, and $\eta$ (in radians) have been defined previously.[15,16]

## Collection and Reduction of Intensity Data

Dark brown, pyramidal crystals of $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ were kindly supplied by Dr. W. R. Roper. On the basis of Weissenberg and precession photography of the $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, and $2kl$ nets we established that the crystals belong to the orthorhombic system. The systematic absences observed for the reflections $0kl$, $k$ odd; $h0l$, $l$ odd are consistent with the space groups $D_{2h}^{11}$-$Pbcm$ or $C_{2v}^{5}$-$Pbc2_1$. On the basis of optical goniometry the faces of the crystal which was chosen for data collection were identified as (001), $(00\bar{1})$, (342), $(\bar{3}42)$, $(\bar{3}\bar{4}2)$, and $(3\bar{4}2)$. Lattice constants were determined at 22.5° from a least-squares refinement of the setting angles of 11 strong reflections centered on a Picker four-circle automatic diffractometer[7] using Mo $K\alpha_1$ radiation ($\lambda$ 0.70930 Å). They are $a$ = 11.335 (9), $b$ = 21.992 (17), and $c$ = 19.170 (15) Å. The density calculated for four formula weights per unit cell is 1.54 g/cm$^3$, which agrees well with that of 1.53 (±0.02) g/cm$^3$ measured by the gradient tube method. With four formula weights in the unit cell either a mirror plane, a twofold axis, or a center of symmetry is imposed on the ions if the centrosymmetric space group $Pbcm$ is correct, but no symmetry is imposed if the space group is the noncentrosymmetric $Pbc2_1$.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter, $\omega$-scan technique. The width at half-height for a typical strong reflection was found to be approximately 0.05°, which is acceptably low.[8] The intensity data were collected as previously described[7] using a crystal with approximate dimensions 0.1 × 0.07 × 0.07 mm. The crystal was mounted on the diffractometer with spindle axis roughly coincident with the $c^*$ reciprocal lattice vector.

For data collection Mo $K\alpha$ radiation was used and the diffracted beams were filtered through 1.0 mil of niobium foil. The intensities were measured by the $\theta$–$2\theta$ technique at a takeoff angle of 1.5°. At this angle the intensity of a reflection was about 80% of the maximum value as a function of takeoff angle. A receiving aperture 4 mm × 4 mm was used and positioned 30 cm from the crystal. A nonsymmetric scan range of $-0.4$ to $+0.6°$ from the $K\alpha_1$ peak for reflections with $\theta < 15°$ and $-0.45$ to $+0.75°$ for the reflections with $15° < \theta < 20°$ was used. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils whose thickness had been chosen to give attenuator factors of approximately 2.3. The pulse height analyzer was set for approximately a 90% window centered on the Mo $K\alpha$ peak.

The intensities of four standard reflections were measured every 200 reflections. They showed deviations of only ±1%. Intensity data were collected for the unique $hkl$ planes up to $\theta(\text{Mo } K\alpha_1) < 20°$. Past this point very few intensities were above background under the conditions of data collection just detailed. The data were processed as previously described.[7] The value of $p$ was chosen as 0.04. Of the 2330 reflections observed, 485 had intensities which were less than their standard deviations. The linear absorption coefficient for the compound for Mo $K\bar{\alpha}$ radiation is 30.8 cm$^{-1}$. The data were corrected for absorption; the transmission coefficients ranged from 0.77 to 0.83.

## Solution and Refinement of Structure

If the correct space group is $Pbcm$, then a twofold axis, a center of symmetry, or mirror plane of symmetry is imposed on the ions of the compound $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$, and probably there would result disorder of the triphenylphosphine groups. Disorder of triphenylphosphine groups has not been observed in the numerous studies of such complexes in these laboratories. Hence the noncentric space group $Pbc2_1$ was assumed.

The iridium atom was located from a three-dimensional Patterson function.[9] The fractional $z$ coordinate of the iridium atom was set at 1/4 to fix the origin of the unit cell. Two cycles of least-squares refinement of scale factor and iridium $x$ and $y$ coordinates yielded

---

(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(8) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(9) In addition to various local programs, those used in this work include local modifications of Hamilton's GONO9 absorption program, Johnson's ORTEP thermal ellipsoid plotting program, and Zalkin's FORDAP Fourier program. Our local least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.

the discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.234 and 0.299, respectively, where the weights $w$ were taken as $4F_o^2/\sigma^2(F_o^2)$. In this and succeeding refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and only the 1342 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. In all calculations of $|F_c|$ the usual tabulation of atomic scattering factors was used for P, Cl, O, N, and C;[10] those for H were from Stewart, Davidson, and Simpson,[11] and those of Cromer and Waber were used for Ir.[12] The effects of anomalous dispersion were included in the calculation of $F_c$;[13] the values of $\Delta f'$ and $\Delta f''$ for Ir, Cl, and P were those given by Cromer.[14] Subsequent difference Fourier maps, interspersed with least-squares refinements, led to positions of all remaining nonhydrogen atoms. The phenyl ring carbon atoms and the perchlorate oxygen atoms were treated as rigid groups[15,16] of $D_{6h}$ ($d$(C–C) = 1.390 Å) and $T_d$ ($d$(Cl–O) = 1.42 Å) symmetry, respectively. The nongroup atoms were assigned isotropic thermal parameters and the least-squares refinement converged to give the discrepancy factors $R_1 = 0.089$ and $R_2 = 0.124$. The nongroup atoms were then assigned anisotropic temperature factors and the phenyl group atoms were assigned individual isotropic temperature factors. Three cycles of least-squares refinement lowered the discrepancy factors to $R_1 = 0.053$ and $R_2 = 0.056$. The positions of the hydrogen atoms were idealized ($d$(C–H) = 0.98 Å) and each hydrogen atom was assigned an isotropic temperature factor of 3.0 Å$^2$. In subsequent structure factor calculations the contributions of these hydrogen atoms were taken into account. After three more cycles the refinement converged to give the discrepancy factors $R_1 = 0.047$ and $R_2 = 0.049$.

There were at this point two possible structures to consider: the enantiomorph A, the structure as hitherto assumed, and enantiomorph B, the mirror image of A reflected across a plane at $z = 1/4$. One cycle of least-squares refinement with $(\bar{h}\bar{k}\bar{l})$ assumed in place of $(hkl)$ gave the discrepancy factors $R_1 = 0.052$ and $R_2 = 0.055$. Hence our original arbitrary choice of enantiomorph A is correct.

An inspection of the data suggests that no correction for secondary extinction is necessary. Moreover, a comparison of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based on $|F_o|$, Miller indices, and the scattering angle shows no unexpected trends. Thus the relative weighting scheme is a reasonable one. The error of an observation of unit weight is 1.23 e$^-$.

The rather high temperature factor of the perchlorate oxygen atoms, 15 Å$^2$, is a result of some disorder of these atoms. Difference Fourier maps indicated that this disorder might take the form of a rotation of the perchlorate group about the Cl–O3 axis. However, trial calculations indicated that the degree of disorder must be less than 20%. Pehaps as a result of this disorder the origin of the oxygen-atom group is 0.12 Å from the chlorine atom. A difference map based on the final parameters contains no peaks higher than 0.89 (13) e$^-$/Å$^3$ and is approximately 25% of the height of a

TABLE II

DERIVED PARAMETERS

| Atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| | (a) Phenyl-Ring Carbon Atoms[a] | | | |
| Ring 1 | | | | |
| R1C1 | 0.1550 (17) | 0.2836 (9) | 0.1422 (11) | 2.0 (7) |
| R1C2 | 0.2291 (20) | 0.2650 (7) | 0.0885 (12) | 4.0 (8) |
| R1C3 | 0.2783 (19) | 0.3077 (11) | 0.0437 (10) | 4.1 (9) |
| R1C4 | 0.2533 (22) | 0.3691 (10) | 0.0526 (12) | 4.6 (10) |
| R1C5 | 0.1792 (23) | 0.3878 (7) | 0.1063 (13) | 5.1 (9) |
| R1C6 | 0.1300 (17) | 0.3450 (11) | 0.1510 (10) | 4.8 (8) |
| Ring 2 | | | | |
| R2C1 | −0.0141 (16) | 0.2690 (7) | 0.2539 (11) | 3.0 (6) |
| R2C2 | −0.1344 (17) | 0.2784 (8) | 0.2449 (10) | 3.5 (6) |
| R2C3 | −0.1967 (13) | 0.3139 (10) | 0.2922 (12) | 5.3 (8) |
| R2C4 | −0.1387 (19) | 0.3400 (9) | 0.3487 (10) | 4.6 (9) |
| R2C5 | −0.0184 (20) | 0.3306 (9) | 0.3578 (9) | 4.4 (8) |
| R2C6 | 0.0439 (13) | 0.2951 (9) | 0.3104 (12) | 3.8 (8) |
| Ring 3 | | | | |
| R3C1 | −0.0315 (15) | 0.2010 (9) | 0.1269 (10) | 3.1 (7) |
| R3C2 | −0.1008 (18) | 0.1505 (9) | 0.1416 (9) | 2.8 (7) |
| R3C3 | −0.1913 (17) | 0.1339 (8) | 0.0965 (11) | 4.4 (8) |
| R3C4 | −0.2126 (16) | 0.1679 (10) | 0.0367 (10) | 4.6 (9) |
| R3C5 | −0.1433 (20) | 0.2185 (10) | 0.0219 (9) | 6.1 (11) |
| R3C6 | −0.0528 (18) | 0.2350 (8) | 0.0670 (12) | 3.2 (8) |
| Ring 4 | | | | |
| R4C1 | −0.0177 (14) | 0.0397 (10) | 0.2819 (10) | 3.6 (8) |
| R4C2 | −0.0632 (19) | −0.0189 (8) | 0.2861 (11) | 4.2 (9) |
| R4C3 | −0.1707 (20) | −0.0290 (7) | 0.3190 (12) | 4.2 (8) |
| R4C4 | −0.2326 (15) | 0.0195 (11) | 0.3478 (11) | 4.8 (9) |
| R4C5 | −0.1870 (19) | 0.0781 (9) | 0.3436 (11) | 4.5 (8) |
| R4C6 | −0.0796 (20) | 0.0882 (7) | 0.3106 (11) | 3.7 (8) |
| Ring 5 | | | | |
| R5C1 | 0.2205 (17) | 0.0100 (8) | 0.3090 (9) | 2.4 (7) |
| R5C2 | 0.3244 (18) | −0.0187 (9) | 0.2891 (8) | 3.6 (7) |
| R5C3 | 0.3940 (14) | −0.0476 (9) | 0.3388 (13) | 4.9 (9) |
| R5C4 | 0.3596 (19) | −0.0476 (10) | 0.4084 (11) | 5.3 (10) |
| R5C5 | 0.2557 (21) | −0.0189 (11) | 0.4284 (8) | 4.3 (9) |
| R5C6 | 0.1862 (15) | 0.0100 (8) | 0.3786 (11) | 3.5 (7) |
| Ring 6 | | | | |
| R6C1 | 0.1340 (19) | 0.0088 (11) | 0.1642 (10) | 4.2 (9) |
| R6C2 | 0.1487 (20) | −0.0539 (11) | 0.1648 (11) | 4.6 (9) |
| R6C3 | 0.1477 (20) | −0.0863 (8) | 0.1026 (15) | 7.0 (12) |
| R6C4 | 0.1321 (21) | −0.0559 (12) | 0.0396 (11) | 6.1 (11) |
| R6C5 | 0.1175 (20) | 0.0069 (12) | 0.0390 (10) | 5.1 (9) |
| R6C6 | 0.1184 (19) | 0.0392 (8) | 0.1013 (13) | 3.6 (8) |
| Ring 7 | | | | |
| R7C1 | 0.4636 (21) | 0.1612 (13) | 0.3271 (10) | 4.1 (8) |
| R7C2 | 0.5399 (24) | 0.2067 (10) | 0.3494 (14) | 6.9 (13) |
| R7C3 | 0.5978 (20) | 0.2011 (10) | 0.4130 (16) | 6.3 (11) |
| R7C4 | 0.5796 (22) | 0.1499 (13) | 0.4542 (11) | 5.6 (9) |
| R7C5 | 0.5033 (24) | 0.1044 (10) | 0.4319 (13) | 4.3 (8) |
| R7C6 | 0.4454 (20) | 0.1100 (11) | 0.3683 (14) | 5.0 (10) |
| Ring 8 | | | | |
| R8C1 | 0.4503 (19) | 0.2327 (8) | 0.2039 (11) | 1.6 (6) |
| R8C2 | 0.4107 (15) | 0.2885 (10) | 0.2287 (8) | 2.6 (8) |
| R8C3 | 0.4607 (20) | 0.3420 (7) | 0.2041 (11) | 4.0 (7) |
| R8C4 | 0.5504 (20) | 0.3398 (9) | 0.1547 (12) | 5.4 (9) |
| R8C5 | 0.5900 (17) | 0.2840 (13) | 0.1299 (10) | 4.9 (9) |
| R8C6 | 0.5400 (20) | 0.2305 (9) | 0.1545 (11) | 4.0 (10) |
| Ring 9 | | | | |
| R9C1 | 0.4674 (21) | 0.1025 (8) | 0.1901 (11) | 3.3 (8) |
| R9C2 | 0.4181 (17) | 0.0885 (10) | 0.1257 (12) | 3.6 (9) |
| R9C3 | 0.4610 (21) | 0.0395 (11) | 0.0875 (9) | 4.2 (9) |
| R9C4 | 0.5531 (22) | 0.0046 (8) | 0.1137 (12) | 5.1 (10) |
| R9C5 | 0.6024 (18) | 0.0187 (9) | 0.1781 (13) | 4.7 (9) |
| R9C6 | 0.5596 (20) | 0.0676 (10) | 0.2163 (9) | 3.1 (8) |
| | (b) Perchlorate Group Oxygen Atoms | | | |
| O2 | 0.367 (3) | 0.389 (1) | 0.391 (2) | 15 (1) |
| O3 | 0.441 (2) | 0.326 (2) | 0.479 (2) | |
| O4 | 0.300 (3) | 0.289 (1) | 0.401 (2) | |
| O5 | 0.247 (3) | 0.361 (2) | 0.485 (2) | |

[a] C1 is attached to P; other carbon atoms are numbered in succession so that C4 is para to C1. R1, R2, and R3 are attached to P1; R4, R5, and R6 to P2; and R7, R8, and R9 to P3.

---

[10] J. A. Ibers, "International Tables of X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, Table 3.3.1 A.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[12] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[13] J. A. Ibers and W. Hamilton, *ibid.*, **17**, 781 (1964).

[14] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[15] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

[16] S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965); S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) IN ELECTRONS FOR $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$

| H | K | FO | FC |
|---|---|---|---|
| ***** L = 0 ***** | | | |
| 0 | 0 | | 22206 |
| 0 | 2 | 2068 | 1904 |
| 0 | 4 | 1234 | 1125 |
| 0 | 6 | 4325 | 4155 |
| 0 | 10 | 2700 | 2661 |
| 0 | 12 | 1586 | 1524 |
| 0 | 14 | 1339 | 1250 |
| 0 | 16 | 2273 | 2323 |
| 0 | 18 | 1232 | 1128 |
| 0 | 20 | 857 | 906 |
| 1 | 0 | 886 | 858 |
| 1 | 1 | 4057 | 3695 |
| 1 | 3 | 372 | 364 |
| 1 | 4 | 986 | 895 |
| 1 | 5 | 3584 | 3452 |
| 1 | 7 | 1379 | 1339 |
| 1 | 9 | 1636 | 1649 |
| 1 | 10 | 888 | 940 |
| 1 | 11 | 1809 | 1827 |
| 1 | 14 | 517 | 459 |
| 1 | 15 | 1301 | 1253 |
| 1 | 17 | 1279 | 1313 |
| 1 | 21 | 991 | 1039 |
| 2 | 0 | 1083 | 1093 |
| 2 | 1 | 594 | 598 |
| 2 | 2 | 426 | 347 |
| 2 | 4 | 1685 | 1677 |
| 2 | 5 | 381 | 297 |
| 2 | 6 | 2607 | 2580 |
| 2 | 7 | 1743 | 1795 |
| 2 | 8 | 433 | 428 |
| 2 | 9 | 1520 | 1494 |
| 2 | 10 | 1213 | 1265 |
| 2 | 12 | 913 | 895 |
| 2 | 14 | 558 | 612 |
| 2 | 15 | 705 | 750 |
| 2 | 16 | 637 | 591 |
| 2 | 20 | 556 | 530 |
| 3 | 0 | 4716 | 4830 |
| 3 | 1 | 822 | 829 |
| 3 | 4 | 1823 | 1797 |
| 3 | 5 | 833 | 824 |
| 3 | 6 | 1743 | 1695 |
| 3 | 10 | 1679 | 1721 |
| 3 | 11 | 681 | 748 |
| 3 | 12 | 1175 | 1218 |
| 3 | 14 | 639 | 686 |
| 3 | 15 | 528 | 445 |
| 3 | 16 | 1075 | 1089 |
| 3 | 18 | 543 | 597 |
| 3 | 20 | 802 | 782 |
| 4 | 0 | 1537 | 1572 |
| 4 | 1 | 1602 | 1596 |
| 4 | 2 | 695 | 593 |
| 4 | 3 | 932 | 965 |
| 4 | 5 | 2304 | 2310 |
| 4 | 7 | 1140 | 1118 |
| 4 | 8 | 745 | 651 |
| 4 | 9 | 1331 | 1335 |
| 4 | 10 | 600 | 597 |
| 4 | 11 | 1596 | 1580 |
| 4 | 13 | 727 | 759 |
| 4 | 15 | 1091 | 1045 |
| 4 | 17 | 1117 | 1097 |
| 5 | 0 | 2742 | 2715 |
| 5 | 1 | 678 | 600 |
| 5 | 2 | 930 | 952 |
| 5 | 4 | 1562 | 1578 |
| 5 | 5 | 852 | 946 |
| 5 | 6 | 2194 | 2135 |
| 5 | 7 | 826 | 908 |
| 5 | 9 | 465 | 453 |
| 5 | 10 | 1352 | 1412 |
| 5 | 11 | 626 | 675 |
| 5 | 12 | 1196 | 1141 |
| 5 | 16 | 1083 | 1141 |
| 6 | 0 | 994 | 1082 |
| 6 | 1 | 955 | 957 |
| 6 | 4 | 1119 | 1127 |
| 6 | 5 | 1659 | 1657 |
| 6 | 6 | 997 | 1077 |
| 6 | 9 | 655 | 637 |
| 6 | 10 | 1097 | 1041 |
| 6 | 11 | 1158 | 1198 |
| 6 | 12 | 535 | 421 |
| 6 | 15 | 1189 | 1190 |
| 6 | 16 | 624 | 580 |
| 6 | 17 | 612 | 596 |
| 7 | 1 | 1040 | 1024 |
| 7 | 2 | 487 | 380 |
| 7 | 4 | 584 | 621 |
| 7 | 5 | 1469 | 1524 |
| 7 | 6 | 578 | 653 |
| 7 | 7 | 764 | 639 |
| 7 | 8 | 551 | 525 |
| 7 | 9 | 850 | 834 |
| 7 | 10 | 596 | 414 |
| 7 | 11 | 877 | 786 |
| 7 | 12 | 702 | 615 |
| 7 | 15 | 1010 | 952 |
| 8 | 0 | 1421 | 1416 |
| 8 | 2 | 832 | 900 |
| 8 | 4 | 946 | 966 |
| 8 | 6 | 1054 | 1054 |
| 8 | 10 | 720 | 774 |
| 8 | 12 | 948 | 821 |
| 8 | 14 | 662 | 573 |
| 9 | 1 | 1034 | 1048 |
| 9 | 5 | 913 | 889 |
| 9 | 9 | 577 | 580 |
| 9 | 11 | 839 | 792 |
| 10 | 0 | 652 | 634 |
| 10 | 1 | 732 | 787 |
| 10 | 4 | 678 | 801 |
| 10 | 5 | 595 | 736 |
| 10 | 6 | 935 | 925 |
| ***** L = 1 ***** | | | |
| 0 | 2 | 3771 | 3462 |
| 0 | 4 | 830 | 857 |
| 0 | 6 | 1141 | 1163 |
| 0 | 8 | 2364 | 2449 |
| 0 | 10 | 994 | 1065 |
| 0 | 12 | 1552 | 1576 |
| 0 | 14 | 1882 | 1895 |
| 0 | 18 | 1067 | 1060 |
| 0 | 20 | 693 | 665 |
| 1 | 1 | 2504 | 2263 |
| 1 | 2 | 615 | 584 |
| 1 | 3 | 1974 | 2005 |
| 1 | 4 | 1279 | 1167 |
| 1 | 5 | 1216 | 1221 |
| 1 | 7 | 1927 | 1944 |
| 1 | 8 | 1310 | 1224 |
| 1 | 9 | 2241 | 2310 |
| 1 | 10 | 458 | 438 |
| 1 | 11 | 475 | 456 |
| 1 | 12 | 729 | 788 |
| 1 | 13 | 1676 | 1755 |
| 1 | 15 | 943 | 955 |
| 1 | 18 | 570 | 508 |
| 1 | 19 | 1247 | 1236 |
| 2 | 1 | 1495 | 1475 |
| 2 | 2 | 864 | 848 |
| 2 | 3 | 3491 | 3429 |
| 2 | 4 | 1490 | 1442 |
| 2 | 5 | 1229 | 1241 |
| 2 | 6 | 1351 | 1319 |
| 2 | 7 | 1028 | 1073 |
| 2 | 8 | 2255 | 2255 |
| 2 | 9 | 1048 | 1073 |
| 2 | 10 | 837 | 850 |
| 2 | 11 | 645 | 658 |
| 2 | 12 | 922 | 874 |
| 2 | 13 | 1264 | 1332 |
| 2 | 14 | 943 | 948 |
| 2 | 18 | 852 | 804 |
| 2 | 19 | 830 | 817 |
| 2 | 20 | 636 | 644 |
| 3 | 1 | 953 | 949 |
| 3 | 2 | 3229 | 3199 |
| 3 | 3 | 768 | 744 |
| 3 | 4 | 1188 | 1234 |
| 3 | 5 | 603 | 559 |
| 3 | 6 | 523 | 600 |
| 3 | 7 | 1198 | 1175 |
| 3 | 8 | 1994 | 2063 |
| 3 | 10 | 570 | 497 |
| 3 | 11 | 490 | 382 |
| 3 | 12 | 1228 | 1179 |
| 3 | 13 | 541 | 437 |
| 3 | 14 | 1253 | 1266 |
| 3 | 17 | 697 | 733 |
| 3 | 18 | 991 | 881 |
| 3 | 20 | 713 | 640 |
| 4 | 1 | 1892 | 1901 |
| 4 | 3 | 2819 | 2826 |
| 4 | 7 | 2224 | 2256 |
| 4 | 9 | 2034 | 1988 |
| 4 | 13 | 1489 | 1482 |
| 4 | 15 | 648 | 716 |
| 4 | 17 | 861 | 827 |
| 4 | 19 | 1166 | 1201 |
| 5 | 1 | 1203 | 1208 |
| 5 | 2 | 1844 | 1900 |
| 5 | 4 | 1554 | 1577 |
| 5 | 6 | 1083 | 1101 |
| 5 | 8 | 2366 | 2402 |
| 5 | 9 | 892 | 884 |
| 5 | 10 | 962 | 951 |
| 5 | 12 | 810 | 836 |
| 5 | 14 | 1436 | 1450 |
| 5 | 18 | 1000 | 911 |
| 6 | 1 | 523 | 483 |
| 6 | 2 | 555 | 589 |
| 6 | 3 | 1790 | 1822 |
| 6 | 4 | 700 | 684 |
| 6 | 5 | 512 | 484 |
| 6 | 6 | 673 | 663 |
| 6 | 7 | 1387 | 1395 |
| 6 | 8 | 1027 | 1090 |
| 6 | 9 | 1067 | 1021 |
| 6 | 13 | 1237 | 1293 |
| 6 | 17 | 602 | 465 |
| 7 | 1 | 536 | 534 |
| 7 | 2 | 767 | 811 |
| 7 | 3 | 1380 | 1402 |
| 7 | 4 | 985 | 1001 |
| 7 | 7 | 1284 | 1316 |
| 7 | 9 | 692 | 679 |
| 7 | 12 | 602 | 558 |
| 7 | 13 | 1015 | 960 |
| 7 | 14 | 829 | 842 |
| 8 | 2 | 1333 | 1297 |
| 8 | 4 | 1130 | 1121 |
| 8 | 6 | 618 | 630 |
| 8 | 8 | 622 | 781 |
| 8 | 12 | 1095 | 1076 |
| 8 | 14 | 1013 | 1053 |
| 9 | 3 | 1366 | 1341 |
| 9 | 4 | 571 | 653 |
| 9 | 7 | 980 | 1006 |
| 9 | 8 | 584 | 427 |
| 9 | 9 | 676 | 652 |
| 10 | 2 | 958 | 992 |
| 10 | 3 | 911 | 891 |
| 10 | 4 | 739 | 690 |
| 10 | 6 | 569 | 435 |
| 10 | 7 | 563 | 569 |
| 10 | 8 | 975 | 1048 |
| ***** L = 2 ***** | | | |
| 0 | 0 | 5245 | 4978 |
| 0 | 2 | 1090 | 1018 |
| 0 | 4 | 1248 | 1182 |
| 0 | 6 | 2710 | 2587 |
| 0 | 8 | 814 | 806 |
| 0 | 10 | 2259 | 2216 |
| 0 | 12 | 1355 | 1421 |
| 0 | 14 | 935 | 902 |
| 0 | 16 | 1752 | 1764 |
| 0 | 18 | 946 | 869 |
| 0 | 20 | 780 | 746 |
| 1 | 0 | 2081 | 1987 |
| 1 | 1 | 2214 | 2157 |
| 1 | 2 | 548 | 556 |
| 1 | 3 | 444 | 405 |
| 1 | 4 | 610 | 540 |
| 1 | 5 | 2213 | 2186 |
| 1 | 6 | 928 | 977 |
| 1 | 7 | 1491 | 1493 |
| 1 | 9 | 1356 | 1314 |
| 1 | 10 | 878 | 867 |
| 1 | 11 | 2014 | 2065 |
| 1 | 12 | 600 | 526 |
| 1 | 15 | 1164 | 1267 |
| 1 | 16 | 520 | 522 |
| 1 | 17 | 1238 | 1287 |
| 2 | 0 | 1290 | 1360 |
| 2 | 1 | 1875 | 1843 |
| 2 | 2 | 555 | 483 |
| 2 | 3 | 880 | 858 |
| 2 | 4 | 1516 | 1508 |
| 2 | 5 | 724 | 704 |
| 2 | 6 | 1810 | 1805 |
| 2 | 7 | 1371 | 1397 |
| 2 | 9 | 1164 | 1203 |
| 2 | 10 | 986 | 1051 |
| 2 | 11 | 1119 | 1177 |
| 2 | 12 | 1071 | 1013 |
| 2 | 15 | 866 | 798 |
| 2 | 16 | 679 | 810 |
| 2 | 17 | 595 | 550 |
| 2 | 20 | 580 | 668 |
| 3 | 0 | 3085 | 3038 |
| 3 | 2 | 1149 | 1196 |
| 3 | 3 | 781 | 734 |
| 3 | 4 | 1967 | 1961 |
| 3 | 5 | 865 | 807 |
| 3 | 6 | 1818 | 1898 |
| 3 | 7 | 580 | 573 |
| 3 | 8 | 453 | 234 |
| 3 | 9 | 408 | 332 |
| 3 | 10 | 1950 | 2022 |
| 3 | 11 | 617 | 622 |
| 3 | 12 | 1096 | 1066 |
| 3 | 13 | 450 | 402 |
| 3 | 14 | 821 | 801 |
| 3 | 16 | 1132 | 1111 |
| 3 | 20 | 889 | 880 |
| 4 | 0 | 735 | 802 |
| 4 | 1 | 2323 | 2353 |
| 4 | 2 | 681 | 634 |
| 4 | 3 | 972 | 905 |
| 4 | 5 | 2835 | 2959 |
| 4 | 7 | 1309 | 1352 |
| 4 | 9 | 1407 | 1391 |
| 4 | 11 | 1760 | 1787 |
| 4 | 15 | 1361 | 1337 |
| 4 | 17 | 984 | 1047 |
| 5 | 0 | 2511 | 2562 |
| 5 | 1 | 619 | 584 |
| 5 | 2 | 787 | 746 |
| 5 | 3 | 744 | 692 |
| 5 | 4 | 1354 | 1353 |
| 5 | 6 | 2109 | 2105 |
| 5 | 7 | 561 | 497 |
| 5 | 10 | 1532 | 1456 |
| 5 | 11 | 650 | 631 |
| 5 | 12 | 1103 | 1098 |
| 5 | 16 | 1217 | 1191 |
| 6 | 0 | 1354 | 1365 |
| 6 | 1 | 1352 | 1437 |
| 6 | 2 | 552 | 456 |
| 6 | 4 | 606 | 691 |
| 6 | 5 | 1670 | 1660 |
| 6 | 6 | 1203 | 1154 |
| 6 | 7 | 824 | 881 |
| 6 | 9 | 666 | 682 |
| 6 | 10 | 957 | 982 |
| 6 | 11 | 1059 | 975 |
| 6 | 12 | 565 | 482 |
| 6 | 15 | 999 | 1025 |
| 7 | 0 | 826 | 799 |
| 7 | 1 | 1063 | 1100 |
| 7 | 2 | 620 | 614 |
| 7 | 5 | 1236 | 1340 |
| 7 | 6 | 868 | 789 |
| 7 | 7 | 488 | 410 |
| 7 | 9 | 792 | 799 |
| 7 | 11 | 874 | 789 |
| 7 | 15 | 833 | 813 |
| 8 | 0 | 1424 | 1520 |
| 8 | 2 | 502 | 567 |
| 8 | 4 | 790 | 872 |
| 8 | 6 | 1057 | 1108 |
| 8 | 10 | 862 | 761 |
| 8 | 12 | 682 | 698 |
| 9 | 0 | 583 | 426 |
| 9 | 1 | 1118 | 1133 |
| 9 | 5 | 1267 | 1280 |
| 9 | 6 | 677 | 597 |
| 9 | 7 | 558 | 550 |
| 9 | 9 | 832 | 819 |
| 9 | 11 | 925 | 882 |
| 10 | 0 | 910 | 973 |
| 10 | 1 | 735 | 678 |
| 10 | 4 | 656 | 652 |
| 10 | 5 | 706 | 681 |
| 10 | 6 | 755 | 893 |
| ***** L = 3 ***** | | | |
| 0 | 2 | 3805 | 3804 |
| 0 | 4 | 1463 | 1534 |
| 0 | 6 | 1598 | 1609 |
| 0 | 8 | 2948 | 2948 |
| 0 | 10 | 1476 | 1312 |
| 0 | 12 | 2219 | 2252 |
| 0 | 14 | 1535 | 1471 |
| 0 | 18 | 1345 | 1304 |
| 0 | 20 | 885 | 899 |
| 1 | 1 | 2175 | 2139 |
| 1 | 2 | 734 | 765 |
| 1 | 3 | 4576 | 4611 |
| 1 | 4 | 1663 | 1630 |
| 1 | 5 | 769 | 825 |
| 1 | 6 | 493 | 519 |
| 1 | 7 | 2420 | 2488 |
| 1 | 8 | 531 | 535 |
| 1 | 9 | 1797 | 1769 |
| 1 | 11 | 912 | 944 |
| 1 | 15 | 798 | 780 |
| 1 | 17 | 591 | 565 |
| 1 | 18 | 553 | 581 |
| 1 | 19 | 1128 | 1176 |
| 2 | 1 | 778 | 779 |
| 2 | 2 | 2570 | 2554 |
| 2 | 4 | 1382 | 1432 |
| 2 | 6 | 723 | 621 |
| 2 | 7 | 625 | 600 |
| 2 | 8 | 1272 | 1305 |
| 2 | 9 | 688 | 804 |
| 2 | 11 | 1210 | 1204 |
| 2 | 12 | 978 | 1008 |
| 2 | 13 | 868 | 953 |
| 2 | 14 | 1083 | 1106 |
| 2 | 18 | 859 | 906 |
| 2 | 19 | 849 | 785 |
| 2 | 20 | 576 | 477 |
| 3 | 1 | 1222 | 1180 |
| 3 | 2 | 1611 | 1601 |
| 3 | 3 | 735 | 668 |
| 3 | 4 | 1238 | 1214 |
| 3 | 6 | 662 | 698 |
| 3 | 7 | 927 | 851 |
| 3 | 8 | 1235 | 1194 |
| 3 | 9 | 907 | 873 |
| 3 | 10 | 433 | 482 |
| 3 | 12 | 1269 | 1315 |
| 3 | 14 | 954 | 980 |
| 3 | 18 | 812 | 818 |
| 3 | 20 | 588 | 624 |
| 4 | 1 | 1319 | 1317 |
| 4 | 2 | 625 | 617 |
| 4 | 3 | 2200 | 2177 |
| 4 | 4 | 612 | 592 |
| 4 | 5 | 668 | 610 |
| 4 | 7 | 2019 | 1965 |
| 4 | 8 | 850 | 792 |
| 4 | 9 | 1500 | 1551 |
| 4 | 13 | 1381 | 1360 |
| 4 | 15 | 638 | 621 |
| 4 | 19 | 1040 | 1001 |
| 5 | 1 | 867 | 805 |
| 5 | 2 | 1798 | 1823 |
| 5 | 3 | 612 | 712 |
| 5 | 4 | 1120 | 1157 |
| 5 | 5 | 455 | 333 |
| 5 | 6 | 1010 | 975 |
| 5 | 7 | 584 | 605 |
| 5 | 8 | 2108 | 2098 |
| 5 | 9 | 776 | 843 |
| 5 | 10 | 609 | 595 |
| 5 | 11 | 460 | 354 |
| 5 | 12 | 866 | 902 |
| 5 | 14 | 1379 | 1421 |
| 5 | 18 | 985 | 967 |
| 6 | 1 | 820 | 888 |
| 6 | 2 | 1168 | 1209 |
| 6 | 3 | 1828 | 1831 |
| 6 | 4 | 741 | 691 |
| 6 | 6 | 628 | 631 |
| 6 | 7 | 1399 | 1396 |
| 6 | 8 | 1106 | 1114 |
| 6 | 9 | 1069 | 1072 |
| 6 | 12 | 872 | 852 |
| 6 | 13 | 1082 | 1116 |
| 6 | 15 | 698 | 678 |
| 7 | 1 | 646 | 721 |
| 7 | 2 | 474 | 585 |
| 7 | 3 | 1340 | 1303 |
| 7 | 4 | 868 | 868 |
| 7 | 7 | 1077 | 1003 |
| 7 | 8 | 569 | 622 |
| 7 | 13 | 1001 | 991 |
| 7 | 14 | 773 | 719 |
| 8 | 2 | 1032 | 1038 |
| 8 | 4 | 1123 | 1086 |
| 8 | 6 | 788 | 759 |
| 8 | 8 | 860 | 823 |
| 8 | 12 | 720 | 798 |
| 8 | 14 | 864 | 878 |
| 9 | 1 | 669 | 662 |
| 9 | 3 | 1225 | 1180 |
| 9 | 7 | 1173 | 1195 |
| 9 | 9 | 961 | 961 |
| 10 | 2 | 605 | 681 |
| 10 | 3 | 811 | 770 |
| 10 | 4 | 651 | 716 |
| ***** L = 4 ***** | | | |
| 0 | 0 | 1186 | 1213 |
| 0 | 2 | 1693 | 1733 |
| 0 | 4 | 1618 | 1602 |
| 0 | 6 | 2047 | 2205 |
| 0 | 8 | 538 | 493 |
| 0 | 10 | 2667 | 2743 |
| 0 | 12 | 1151 | 1177 |
| 0 | 14 | 723 | 814 |
| 0 | 16 | 1268 | 1299 |
| 0 | 18 | 760 | 691 |
| 1 | 0 | 2944 | 2806 |
| 1 | 1 | 2242 | 2233 |
| 1 | 2 | 417 | 358 |
| 1 | 3 | 1144 | 1145 |
| 1 | 4 | 757 | 774 |
| 1 | 5 | 2384 | 2512 |
| 1 | 7 | 1519 | 1553 |
| 1 | 9 | 1367 | 1429 |
| 1 | 10 | 451 | 498 |
| 1 | 11 | 2036 | 2017 |
| 1 | 15 | 1140 | 1154 |
| 1 | 16 | 528 | 416 |
| 1 | 17 | 1089 | 973 |
| 2 | 0 | 2276 | 2249 |
| 2 | 2 | 1131 | 1200 |
| 2 | 3 | 1930 | 1889 |
| 2 | 4 | 1642 | 1730 |
| 2 | 5 | 1509 | 1522 |
| 2 | 6 | 1796 | 1851 |
| 2 | 7 | 485 | 416 |
| 2 | 9 | 1002 | 955 |
| 2 | 10 | 1107 | 1153 |
| 2 | 11 | 1374 | 1354 |
| 2 | 12 | 843 | 810 |
| 2 | 14 | 541 | 461 |
| 2 | 15 | 621 | 631 |
| 2 | 16 | 952 | 940 |
| 2 | 20 | 627 | 687 |
| 3 | 0 | 1407 | 1474 |
| 3 | 1 | 783 | 863 |
| 3 | 2 | 1015 | 952 |
| 3 | 3 | 1114 | 1110 |
| 3 | 4 | 1464 | 1443 |
| 3 | 5 | 892 | 887 |
| 3 | 6 | 1465 | 1507 |
| 3 | 7 | 567 | 607 |
| 3 | 8 | 454 | 389 |
| 3 | 9 | 524 | 454 |
| 3 | 10 | 1752 | 1716 |
| 3 | 12 | 725 | 697 |
| 3 | 14 | 694 | 663 |
| 3 | 16 | 870 | 934 |
| 4 | 0 | 965 | 971 |
| 4 | 1 | 2003 | 2062 |
| 4 | 2 | 478 | 544 |
| 4 | 4 | 463 | 497 |
| 4 | 5 | 2113 | 2081 |
| 4 | 6 | 594 | 572 |
| 4 | 7 | 1138 | 1094 |
| 4 | 9 | 1310 | 1375 |
| 4 | 11 | 1791 | 1756 |
| 4 | 15 | 1267 | 1249 |
| 4 | 17 | 949 | 972 |
| 5 | 0 | 1833 | 1832 |
| 5 | 2 | 1344 | 1260 |
| 5 | 3 | 891 | 879 |
| 5 | 4 | 1576 | 1565 |
| 5 | 5 | 520 | 531 |
| 5 | 6 | 2065 | 2019 |
| 5 | 7 | 441 | 474 |
| 5 | 10 | 1737 | 1789 |
| 5 | 11 | 778 | 889 |
| 5 | 12 | 1187 | 1159 |
| 5 | 16 | 1294 | 1350 |
| 6 | 0 | 780 | 873 |
| 6 | 1 | 1303 | 1313 |
| 6 | 4 | 509 | 465 |
| 6 | 5 | 1413 | 1463 |
| 6 | 6 | 590 | 595 |
| 6 | 7 | 843 | 800 |
| 6 | 9 | 660 | 603 |
| 6 | 10 | 842 | 871 |
| 6 | 11 | 936 | 895 |
| 6 | 15 | 877 | 945 |
| 6 | 16 | 723 | 672 |
| 6 | 17 | 653 | 648 |
| 7 | 0 | 550 | 699 |
| 7 | 1 | 823 | 884 |
| 7 | 4 | 661 | 660 |
| 7 | 5 | 1256 | 1238 |
| 7 | 6 | 964 | 985 |
| 7 | 11 | 989 | 988 |
| 7 | 15 | 821 | 770 |
| 8 | 0 | 1063 | 1009 |
| 8 | 4 | 879 | 970 |
| 8 | 6 | 1175 | 1275 |
| 8 | 10 | 1003 | 968 |
| 8 | 12 | 662 | 701 |
| 9 | 1 | 1014 | 1033 |
| 9 | 4 | 558 | 492 |
| 9 | 5 | 1084 | 1197 |
| 9 | 9 | 656 | 658 |
| 9 | 11 | 806 | 824 |
| 10 | 0 | 1023 | 1027 |
| 10 | 2 | 595 | 476 |
| 10 | 4 | 696 | 584 |
| 10 | 5 | 733 | 641 |
| 10 | 6 | 942 | 883 |
| ***** L = 5 ***** | | | |
| 0 | 2 | 2114 | 2176 |
| 0 | 4 | 1544 | 1344 |
| 0 | 6 | 1272 | 1204 |
| 0 | 8 | 3061 | 2926 |
| 0 | 10 | 1283 | 1408 |
| 0 | 12 | 1789 | 1791 |
| 0 | 14 | 959 | 1033 |
| 0 | 18 | 1557 | 1676 |
| 0 | 20 | 818 | 826 |
| 1 | 1 | 1508 | 1532 |
| 1 | 2 | 1133 | 1066 |
| 1 | 3 | 1077 | 1099 |
| 1 | 4 | 749 | 757 |
| 1 | 5 | 540 | 458 |
| 1 | 7 | 1429 | 1340 |
| 1 | 8 | 701 | 836 |
| 1 | 9 | 1550 | 1522 |
| 1 | 11 | 698 | 585 |
| 1 | 12 | 458 | 446 |
| 1 | 13 | 1448 | 1433 |
| 1 | 15 | 696 | 667 |
| 1 | 17 | 839 | 791 |
| 1 | 18 | 571 | 485 |
| 1 | 19 | 1159 | 1054 |
| 2 | 1 | 2084 | 2087 |
| 2 | 2 | 1097 | 1097 |
| 2 | 3 | 2030 | 2111 |
| 2 | 4 | 1454 | 1382 |
| 2 | 5 | 588 | 567 |
| 2 | 6 | 416 | 497 |
| 2 | 7 | 669 | 824 |
| 2 | 8 | 896 | 894 |
| 2 | 9 | 1442 | 1443 |
| 2 | 11 | 768 | 838 |
| 2 | 12 | 1033 | 1083 |
| 2 | 13 | 1009 | 1025 |
| 2 | 14 | 1014 | 928 |
| 2 | 17 | 809 | 755 |
| 2 | 18 | 793 | 862 |
| 2 | 19 | 919 | 925 |
| 3 | 1 | 638 | 541 |
| 3 | 2 | 2402 | 2422 |
| 3 | 3 | 647 | 709 |
| 3 | 4 | 1112 | 1223 |
| 3 | 5 | 739 | 723 |
| 3 | 6 | 603 | 659 |
| 3 | 7 | 482 | 513 |
| 3 | 8 | 2023 | 2077 |
| 3 | 12 | 1411 | 1443 |
| 3 | 13 | 677 | 709 |
| 3 | 14 | 978 | 956 |
| 3 | 18 | 1154 | 1123 |
| 4 | 1 | 1068 | 1089 |
| 4 | 3 | 1825 | 1926 |
| 4 | 5 | 683 | 640 |
| 4 | 6 | 631 | 644 |
| 4 | 7 | 1517 | 1501 |
| 4 | 9 | 1314 | 1364 |
| 4 | 11 | 638 | 690 |
| 4 | 13 | 1524 | 1544 |
| 4 | 15 | 776 | 745 |
| 4 | 17 | 676 | 698 |
| 5 | 1 | 721 | 733 |
| 5 | 2 | 2107 | 2106 |
| 5 | 3 | 882 | 824 |
| 5 | 4 | 1854 | 1876 |
| 5 | 6 | 855 | 884 |
| 5 | 8 | 2021 | 2034 |
| 5 | 9 | 752 | 775 |
| 5 | 10 | 521 | 636 |
| 5 | 12 | 1154 | 1143 |
| 5 | 14 | 1305 | 1282 |
| 6 | 1 | 603 | 597 |
| 6 | 2 | 1056 | 1038 |
| 6 | 3 | 1648 | 1664 |
| 6 | 4 | 606 | 572 |
| 6 | 7 | 1391 | 1360 |
| 6 | 8 | 774 | 739 |
| 6 | 9 | 949 | 960 |
| 6 | 12 | 616 | 662 |
| 6 | 14 | 570 | 474 |
| 7 | 3 | 1068 | 1109 |
| 7 | 4 | 576 | 632 |
| 7 | 6 | 541 | 471 |
| 7 | 13 | 854 | 782 |
| 8 | 2 | 974 | 894 |
| 8 | 4 | 1026 | 973 |
| 8 | 6 | 716 | 723 |
| 8 | 7 | 555 | 333 |
| 8 | 8 | 1037 | 1039 |
| 8 | 12 | 863 | 718 |
| 9 | 1 | 606 | 533 |
| 9 | 3 | 1242 | 1191 |
| 9 | 7 | 1213 | 1212 |
| 9 | 9 | 1010 | 937 |
| 10 | 2 | 880 | 892 |
| 10 | 3 | 786 | 726 |
| 10 | 4 | 724 | 693 |
| ***** L = 6 ***** | | | |
| 0 | 0 | 2772 | 2754 |
| 0 | 2 | 953 | 967 |
| 0 | 4 | 1888 | 1852 |
| 0 | 6 | 1630 | 1734 |
| 0 | 10 | 2169 | 2218 |
| 0 | 12 | 743 | 731 |
| 0 | 14 | 699 | 509 |
| 0 | 16 | 1267 | 1225 |
| 0 | 18 | 556 | 598 |
| 0 | 20 | 897 | 992 |
| 1 | 0 | 448 | 519 |
| 1 | 1 | 2468 | 2461 |
| 1 | 3 | 998 | 1000 |
| 1 | 4 | 454 | 465 |
| 1 | 5 | 1957 | 2032 |
| 1 | 7 | 1444 | 1432 |
| 1 | 9 | 1099 | 1168 |
| 1 | 10 | 834 | 861 |
| 1 | 11 | 2027 | 2107 |
| 1 | 12 | 490 | 365 |
| 1 | 15 | 858 | 969 |
| 1 | 17 | 1157 | 1123 |
| 2 | 0 | 2111 | 2138 |
| 2 | 1 | 864 | 832 |
| 2 | 2 | 1434 | 1466 |
| 2 | 3 | 1220 | 1220 |
| 2 | 4 | 1458 | 1451 |
| 2 | 5 | 900 | 869 |
| 2 | 6 | 1409 | 1425 |
| 2 | 7 | 850 | 790 |
| 2 | 9 | 507 | 437 |
| 2 | 10 | 1263 | 1304 |
| 2 | 11 | 1164 | 1227 |
| 2 | 12 | 827 | 795 |
| 2 | 16 | 983 | 997 |
| 3 | 0 | 949 | 935 |
| 3 | 1 | 1086 | 1061 |
| 3 | 3 | 762 | 708 |
| 3 | 4 | 1517 | 1509 |
| 3 | 5 | 652 | 705 |
| 3 | 6 | 1054 | 1102 |
| 3 | 10 | 1285 | 1290 |
| 3 | 12 | 530 | 475 |
| 3 | 15 | 586 | 629 |
| 3 | 16 | 616 | 786 |
| 4 | 1 | 1917 | 1954 |
| 4 | 4 | 694 | 629 |
| 4 | 5 | 1263 | 1200 |
| 4 | 7 | 897 | 886 |
| 4 | 9 | 1142 | 1114 |
| 4 | 11 | 1407 | 1403 |
| 4 | 15 | 1107 | 1041 |
| 4 | 17 | 1021 | 979 |
| 5 | 0 | 1970 | 2040 |
| 5 | 1 | 1047 | 1056 |
| 5 | 2 | 1300 | 1434 |
| 5 | 4 | 1522 | 1487 |
| 5 | 5 | 530 | 589 |
| 5 | 6 | 1595 | 1592 |
| 5 | 9 | 516 | 410 |
| 5 | 10 | 1353 | 1382 |
| 5 | 11 | 808 | 703 |
| 5 | 12 | 1119 | 1067 |
| 5 | 14 | 645 | 653 |
| 5 | 16 | 1142 | 1193 |
| 6 | 0 | 1314 | 1307 |
| 6 | 1 | 1046 | 1049 |
| 6 | 2 | 493 | 473 |
| 6 | 4 | 810 | 835 |
| 6 | 5 | 1676 | 1808 |
| 6 | 6 | 534 | 665 |
| 6 | 7 | 501 | 498 |
| 6 | 9 | 607 | 619 |
| 6 | 10 | 939 | 889 |
| 6 | 11 | 951 | 999 |
| 6 | 13 | 601 | 637 |
| 6 | 15 | 989 | 951 |
| 7 | 0 | 651 | 659 |
| 7 | 1 | 834 | 789 |
| 7 | 4 | 713 | 755 |
| 7 | 5 | 1255 | 1256 |
| 7 | 6 | 949 | 907 |
| 7 | 11 | 958 | 869 |
| 8 | 0 | 776 | 829 |
| 8 | 4 | 969 | 1025 |
| 8 | 6 | 1318 | 1362 |
| 8 | 10 | 866 | 835 |
| 8 | 12 | 592 | 66 |
| 9 | 1 | 894 | 891 |
| 9 | 5 | 1295 | 1160 |
| 10 | 0 | 892 | 955 |
| 10 | 5 | 624 | 664 |
| ***** L = 7 ***** | | | |
| 0 | 2 | 2773 | 2773 |
| 0 | 4 | 1269 | 1242 |
| 0 | 6 | 1051 | 1082 |
| 0 | 8 | 3426 | 3463 |
| 0 | 10 | 1487 | 1453 |
| 0 | 12 | 1121 | 1150 |
| 0 | 14 | 562 | 524 |
| 0 | 18 | 1509 | 1449 |
| 1 | 1 | 1972 | 1886 |
| 1 | 2 | 833 | 871 |
| 1 | 3 | 2548 | 2535 |
| 1 | 5 | 487 | 408 |
| 1 | 7 | 1626 | 1685 |
| 1 | 8 | 1131 | 1127 |
| 1 | 9 | 2057 | 2057 |
| 1 | 11 | 517 | 514 |
| 1 | 13 | 1368 | 1379 |
| 1 | 15 | 792 | 741 |
| 1 | 17 | 890 | 871 |
| 1 | 19 | 954 | 968 |
| 2 | 1 | 903 | 1007 |
| 2 | 2 | 1668 | 1692 |
| 2 | 3 | 1045 | 1052 |
| 2 | 4 | 1142 | 1148 |
| 2 | 5 | 456 | 313 |
| 2 | 6 | 802 | 760 |
| 2 | 7 | 653 | 625 |
| 2 | 8 | 1120 | 1214 |
| 2 | 9 | 1010 | 1056 |
| 2 | 12 | 1190 | 1196 |
| 2 | 14 | 995 | 1006 |
| 2 | 17 | 661 | 603 |
| 2 | 19 | 646 | 640 |
| 3 | 1 | 961 | 879 |
| 3 | 2 | 1661 | 1696 |
| 3 | 3 | 781 | 782 |
| 3 | 4 | 738 | 700 |
| 3 | 5 | 516 | 535 |
| 3 | 6 | 472 | 535 |
| 3 | 7 | 726 | 776 |
| 3 | 8 | 2060 | 1984 |
| 3 | 12 | 1216 | 1248 |
| 3 | 13 | 736 | 662 |
| 3 | 14 | 931 | 869 |
| 3 | 18 | 860 | 858 |
| 4 | 1 | 1237 | 1157 |
| 4 | 3 | 2019 | 2000 |
| 4 | 5 | 737 | 591 |
| 4 | 7 | 1328 | 1321 |
| 4 | 8 | 482 | 569 |
| 4 | 9 | 1353 | 1309 |
| 4 | 11 | 622 | 522 |
| 4 | 13 | 1513 | 1539 |
| 4 | 15 | 754 | 790 |
| 4 | 17 | 617 | 730 |
| 5 | 1 | 640 | 620 |
| 5 | 2 | 1569 | 1597 |
| 5 | 3 | 585 | 624 |
| 5 | 4 | 1495 | 1462 |
| 5 | 5 | 485 | 364 |
| 5 | 6 | 815 | 798 |
| 5 | 8 | 1390 | 1289 |
| 5 | 9 | 588 | 446 |
| 5 | 12 | 927 | 922 |
| 5 | 13 | 704 | 626 |
| 5 | 14 | 1316 | 1269 |
| 6 | 1 | 646 | 670 |
| 6 | 2 | 801 | 816 |
| 6 | 3 | 1215 | 1227 |
| 6 | 4 | 568 | 620 |
| 6 | 7 | 1372 | 1400 |
| 6 | 8 | 863 | 908 |
| 6 | 9 | 845 | 891 |
| 6 | 12 | 795 | 733 |
| 6 | 13 | 1133 | 1175 |
| 7 | 3 | 963 | 916 |
| 7 | 4 | 617 | 771 |
| 7 | 6 | 702 | 564 |
| 7 | 7 | 834 | 877 |
| 7 | 8 | 542 | 521 |
| 7 | 9 | 606 | 667 |
| 7 | 13 | 1005 | 924 |
| 7 | 14 | 550 | 493 |
| 8 | 2 | 896 | 848 |
| 8 | 4 | 856 | 861 |
| 8 | 6 | 586 | 665 |
| 8 | 8 | 1034 | 1041 |
| 9 | 3 | 969 | 1010 |
| 9 | 7 | 1031 | 1056 |
| 10 | 2 | 802 | 777 |
| ***** L = 8 ***** | | | |
| 0 | 0 | 2027 | 2073 |
| 0 | 2 | 875 | 822 |
| 0 | 4 | 1905 | 1960 |
| 0 | 6 | 1977 | 1896 |
| 0 | 10 | 1564 | 1598 |
| 0 | 12 | 725 | 821 |
| 0 | 14 | 670 | 693 |
| 0 | 16 | 1149 | 1107 |
| 1 | 0 | 1469 | 1364 |
| 1 | 1 | 1537 | 1515 |
| 1 | 3 | 1031 | 998 |
| 1 | 4 | 904 | 874 |
| 1 | 5 | 1709 | 1612 |
| 1 | 6 | 923 | 1006 |
| 1 | 7 | 1206 | 1183 |
| 1 | 9 | 903 | 784 |
| 1 | 10 | 986 | 1023 |
| 1 | 11 | 1587 | 1512 |
| 1 | 15 | 896 | 835 |
| 1 | 17 | 887 | 875 |
| 2 | 0 | 1612 | 1658 |
| 2 | 1 | 1038 | 1047 |
| 2 | 2 | 802 | 796 |
| 2 | 3 | 827 | 816 |
| 2 | 4 | 1152 | 1115 |
| 2 | 5 | 1247 | 1337 |
| 2 | 6 | 955 | 861 |
| 2 | 7 | 785 | 876 |
| 2 | 9 | 681 | 769 |
| 2 | 10 | 1130 | 1148 |
| 2 | 11 | 1241 | 1254 |
| 2 | 12 | 632 | 669 |
| 2 | 15 | 715 | 641 |
| 2 | 16 | 892 | 989 |
| 2 | 17 | 601 | 522 |
| 3 | 0 | 2115 | 2171 |
| 3 | 1 | 888 | 975 |
| 3 | 2 | 757 | 754 |
| 3 | 3 | 674 | 705 |
| 3 | 4 | 1184 | 1160 |
| 3 | 5 | 703 | 705 |
| 3 | 6 | 1514 | 1569 |
| 3 | 9 | 556 | 469 |
| 3 | 10 | 1491 | 1537 |
| 3 | 12 | 599 | 675 |
| 3 | 14 | 837 | 835 |
| 3 | 15 | 632 | 669 |
| 3 | 16 | 1046 | 980 |
| 3 | 17 | 602 | 495 |
| 4 | 0 | 769 | 666 |
| 4 | 1 | 2192 | 2116 |
| 4 | 3 | 566 | 472 |
| 4 | 5 | 1975 | 1972 |
| 4 | 7 | 1005 | 1021 |
| 4 | 9 | 973 | 895 |
| 4 | 11 | 1404 | 1456 |
| 4 | 15 | 1179 | 1143 |
| 4 | 17 | 904 | 892 |
| 5 | 0 | 2275 | 2290 |
| 5 | 1 | 846 | 912 |
| 5 | 2 | 1044 | 1066 |
| 5 | 4 | 1302 | 1357 |
| 5 | 6 | 1346 | 1333 |
| 5 | 10 | 1104 | 1064 |
| 5 | 12 | 1042 | 1032 |
| 5 | 16 | 1175 | 1184 |
| 6 | 0 | 1104 | 1164 |
| 6 | 1 | 1092 | 1102 |
| 6 | 2 | 519 | 514 |
| 6 | 3 | 470 | 239 |
| 6 | 5 | 1522 | 1506 |
| 6 | 6 | 507 | 482 |
| 6 | 7 | 534 | 478 |
| 6 | 9 | 659 | 745 |
| 6 | 10 | 609 | 674 |
| 6 | 11 | 1026 | 1027 |
| 6 | 15 | 765 | 784 |
| 7 | 1 | 571 | 633 |
| 7 | 4 | 722 | 662 |
| 7 | 5 | 1047 | 1032 |
| 7 | 6 | 868 | 854 |
| 7 | 9 | 710 | 607 |
| 7 | 11 | 763 | 724 |
| 8 | 0 | 652 | 690 |
| 8 | 4 | 949 | 965 |
| 8 | 6 | 1098 | 1133 |
| 9 | 1 | 1007 | 984 |
| 9 | 5 | 1233 | 1207 |
| ***** L = 9 ***** | | | |
| 0 | 2 | 2033 | 2115 |
| 0 | 4 | 953 | 1032 |
| 0 | 6 | 746 | 832 |
| 0 | 8 | 2396 | 2552 |
| 0 | 10 | 1090 | 1106 |
| 0 | 12 | 914 | 908 |
| 0 | 14 | 1078 | 1022 |
| 0 | 18 | 1171 | 1122 |
| 1 | 1 | 1239 | 1260 |
| 1 | 2 | 584 | 602 |
| 1 | 3 | 1672 | 1752 |
| 1 | 7 | 1413 | 1498 |
| 1 | 8 | 756 | 716 |
| 1 | 9 | 1517 | 1577 |
| 1 | 11 | 499 | 465 |
| 1 | 13 | 1298 | 1296 |
| 1 | 15 | 545 | 546 |
| 1 | 17 | 609 | 544 |
| 1 | 18 | 560 | 464 |
| 2 | 1 | 969 | 983 |
| 2 | 2 | 1571 | 1616 |
| 2 | 3 | 507 | 459 |
| 2 | 4 | 765 | 842 |
| 2 | 7 | 924 | 889 |
| 2 | 8 | 1044 | 1159 |
| 2 | 9 | 979 | 976 |
| 2 | 12 | 829 | 873 |
| 2 | 14 | 1169 | 1240 |
| 2 | 18 | 610 | 537 |
| 3 | 2 | 1491 | 1472 |
| 3 | 3 | 903 | 879 |
| 3 | 4 | 924 | 897 |
| 3 | 7 | 440 | 327 |
| 3 | 8 | 1349 | 1344 |
| 3 | 11 | 538 | 567 |
| 3 | 12 | 1063 | 1046 |
| 3 | 14 | 821 | 902 |
| 3 | 15 | 558 | 545 |
| 4 | 1 | 1168 | 1131 |
| 4 | 3 | 1677 | 1699 |
| 4 | 4 | 519 | 485 |
| 4 | 7 | 1424 | 1426 |
| 4 | 8 | 463 | 380 |
| 4 | 9 | 1133 | 1171 |
| 4 | 13 | 1252 | 1256 |
| 4 | 15 | 606 | 587 |
| 5 | 1 | 699 | 665 |
| 5 | 2 | 1758 | 1701 |
| 5 | 4 | 1180 | 1188 |
| 5 | 6 | 626 | 704 |
| 5 | 8 | 1250 | 1213 |
| 5 | 9 | 518 | 348 |
| 5 | 10 | 756 | 612 |
| 5 | 12 | 854 | 779 |
| 5 | 14 | 1042 | 1193 |
| 6 | 1 | 658 | 590 |
| 6 | 2 | 863 | 879 |
| 6 | 3 | 1531 | 1511 |
| 6 | 4 | 653 | 547 |
| 6 | 7 | 1028 | 982 |
| 6 | 8 | 727 | 684 |
| 6 | 9 | 627 | 632 |
| 6 | 12 | 586 | 633 |
| 6 | 13 | 918 | 881 |
| 7 | | 735 | 636 |
| 7 | 3 | 988 | 1106 |
| 7 | 4 | 799 | 804 |
| 7 | 7 | 1194 | 1222 |
| 7 | 8 | 589 | 741 |
| 7 | 9 | 655 | 697 |
| 8 | 2 | 983 | 994 |
| 8 | 4 | 823 | 838 |
| 8 | 6 | 785 | 613 |
| 8 | 8 | 952 | 994 |
| 8 | 10 | 539 | 334 |
| 9 | 1 | 578 | 580 |
| 9 | 3 | 960 | 911 |
| ***** L = 10 ***** | | | |
| 0 | 0 | 2515 | 2400 |
| 0 | 2 | 932 | 957 |
| 0 | 4 | 1883 | 1848 |
| 0 | 6 | 2200 | 2184 |
| 0 | 8 | 739 | 713 |
| 0 | 10 | 2131 | 2168 |
| 0 | 12 | 1127 | 1106 |
| 0 | 14 | 897 | 795 |
| 0 | 16 | 1140 | 1162 |
| 1 | 0 | 747 | 907 |
| 1 | 1 | 1542 | 1469 |
| 1 | 3 | 748 | 671 |
| 1 | 5 | 2019 | 2080 |
| 1 | 6 | 474 | 496 |
| 1 | 7 | 1052 | 1072 |
| 1 | 9 | 793 | 796 |
| 1 | 10 | 734 | 745 |
| 1 | 11 | 1470 | 1481 |
| 1 | 12 | 529 | 395 |
| 1 | 15 | 642 | 666 |
| 1 | 16 | 564 | 233 |
| 1 | 17 | 778 | 685 |
| 2 | 0 | 1444 | 1423 |
| 2 | 1 | 820 | 793 |
| 2 | 3 | 526 | 548 |
| 2 | 4 | 955 | 971 |
| 2 | 5 | 1068 | 1090 |
| 2 | 6 | 1119 | 1125 |
| 2 | 9 | 544 | 497 |
| 2 | 10 | 976 | 1025 |
| 2 | 11 | 859 | 901 |
| 2 | 12 | 577 | 573 |
| 2 | 14 | 671 | 526 |
| 2 | 16 | 758 | 842 |
| 3 | 0 | 1596 | 1659 |
| 3 | 1 | 1081 | 1117 |
| 3 | 3 | 470 | 339 |
| 3 | 4 | 919 | 867 |
| 3 | 5 | 802 | 795 |
| 3 | 6 | 1219 | 1205 |
| 3 | 9 | 598 | 559 |
| 3 | 10 | 1140 | 1212 |
| 3 | 14 | 739 | 686 |
| 3 | 16 | 948 | 902 |
| 4 | 0 | 599 | 680 |
| 4 | 1 | 1286 | 1405 |
| 4 | 5 | 1500 | 1473 |
| 4 | 7 | 635 | 675 |
| 4 | 9 | 677 | 742 |
| 4 | 11 | 1136 | 1176 |
| 4 | 15 | 850 | 903 |
| 5 | 0 | 1619 | 1583 |
| 5 | 1 | 1108 | 1094 |
| 5 | 2 | 838 | 798 |
| 5 | 4 | 971 | 994 |
| 5 | 6 | 1229 | 1201 |
| 5 | 9 | 648 | 584 |
| 5 | 10 | 1174 | 1160 |
| 5 | 12 | 911 | 931 |
| 6 | 0 | 1070 | 1052 |
| 6 | 1 | 1085 | 1058 |
| 6 | 2 | 545 | 584 |
| 6 | 5 | 1255 | 1353 |
| 6 | 6 | 611 | 489 |
| 6 | 9 | 604 | 594 |
| 6 | 10 | 804 | 728 |
| 6 | 11 | 927 | 943 |
| 6 | 12 | 677 | 450 |
| 7 | 1 | 727 | 629 |
| 7 | 4 | 687 | 638 |
| 7 | 5 | 1132 | 1029 |
| 7 | 6 | 619 | 585 |
| 7 | 7 | 549 | 463 |
| 7 | 9 | 669 | 674 |
| 7 | 11 | 612 | 703 |
| 8 | 0 | 589 | 542 |
| 8 | 4 | 828 | 892 |
| 8 | 6 | 779 | 894 |
| 9 | 1 | 855 | 813 |
| ***** L = 11 ***** | | | |
| 0 | 2 | 1740 | 1773 |
| 0 | 4 | 990 | 1015 |
| 0 | 6 | 840 | 834 |
| 0 | 8 | 1772 | 1761 |
| 0 | 10 | 1071 | 1095 |
| 0 | 12 | 815 | 790 |
| 0 | 14 | 786 | 814 |
| 1 | 1 | 998 | 1056 |
| 1 | 2 | 453 | 453 |
| 1 | 3 | 1683 | 1654 |
| 1 | 7 | 1194 | 1214 |
| 1 | 8 | 568 | 663 |
| 1 | 9 | 1473 | 1440 |
| 1 | 13 | 919 | 976 |
| 1 | 15 | 581 | 477 |
| 2 | 1 | 908 | 867 |
| 2 | 2 | 1185 | 1200 |
| 2 | 3 | 1156 | 1147 |
| 2 | 4 | 783 | 658 |
| 2 | 6 | 534 | 371 |
| 2 | 7 | 770 | 759 |
| 2 | 8 | 907 | 874 |
| 2 | 9 | 832 | 776 |
| 2 | 10 | 521 | 424 |
| 2 | 12 | 684 | 697 |
| 2 | 13 | 819 | 831 |
| 2 | 14 | 737 | 692 |
| 3 | 2 | 1767 | 1705 |
| 3 | 3 | 749 | 842 |
| 3 | 4 | 890 | 850 |
| 3 | 6 | 651 | 621 |
| 3 | 7 | 663 | 613 |
| 3 | 8 | 1391 | 1378 |
| 3 | 9 | 532 | 541 |
| 3 | 12 | 950 | 951 |
| 3 | 13 | 545 | 512 |
| 3 | 14 | 723 | 730 |
| 4 | 1 | 1018 | 985 |
| 4 | 3 | 1819 | 1783 |
| 4 | 7 | 1373 | 1494 |
| 4 | 9 | 1431 | 1406 |
| 4 | 13 | 1343 | 1255 |
| 4 | 15 | 597 | 598 |
| 5 | 2 | 1384 | 1362 |
| 5 | 3 | 582 | 445 |
| 5 | 4 | 1272 | 1276 |
| 5 | 6 | 676 | 693 |
| 5 | 8 | 1245 | 1198 |
| 5 | 12 | 877 | 781 |
| 5 | 14 | 982 | 989 |
| 6 | 2 | 807 | 785 |
| 6 | 3 | 1150 | 1266 |
| 6 | 7 | 896 | 800 |
| 6 | 8 | 604 | 519 |
| 7 | 1 | 568 | 505 |
| 7 | 3 | 896 | 988 |
| 7 | 7 | 783 | 878 |
| 7 | 9 | 625 | 622 |
| 8 | 2 | 946 | 869 |
| 8 | 4 | 770 | 870 |
| ***** L = 12 ***** | | | |
| 0 | 0 | 1900 | 1922 |
| 0 | 2 | 580 | 556 |
| 0 | 4 | 1118 | 1117 |
| 0 | 6 | 1348 | 1320 |
| 0 | 8 | 504 | 439 |
| 0 | 10 | 1816 | 1864 |
| 0 | 12 | 717 | 745 |
| 0 | 16 | 1156 | 1064 |
| 1 | 0 | 706 | 687 |
| 1 | 1 | 1300 | 1375 |
| 1 | 4 | 663 | 496 |
| 1 | 5 | 1510 | 1530 |
| 1 | 7 | 1044 | 1066 |
| 1 | 9 | 749 | 770 |
| 1 | 10 | 677 | 620 |
| 1 | 11 | 1390 | 1457 |
| 1 | 15 | 705 | 681 |
| 2 | 0 | 1351 | 1349 |
| 2 | 1 | 995 | 985 |
| 2 | 3 | 516 | 572 |
| 2 | 4 | 754 | 835 |
| 2 | 5 | 825 | 803 |
| 2 | 6 | 806 | 836 |
| 2 | 7 | 661 | 649 |
| 2 | 10 | 948 | 928 |
| 2 | 11 | 689 | 852 |
| 3 | 0 | 1687 | 1479 |
| 3 | 1 | 698 | 612 |
| 3 | 4 | 902 | 1014 |
| 3 | 5 | 615 | 662 |
| 3 | 6 | 1176 | 1171 |
| 3 | 10 | 1233 | 1179 |
| 3 | 15 | 552 | 380 |
| 4 | 1 | 1310 | 1311 |
| 4 | 5 | 1484 | 1463 |
| 4 | 7 | 852 | 869 |
| 4 | 9 | 876 | 766 |
| 4 | 11 | 1207 | 1224 |
| 5 | 0 | 1270 | 1311 |
| 5 | 2 | 694 | 611 |
| 5 | 4 | 942 | 917 |
| 5 | 6 | 1205 | 1198 |
| 5 | 10 | 1063 | 1046 |
| 5 | 12 | 728 | 758 |
| 6 | 0 | 993 | 1020 |
| 6 | 1 | 1082 | 1018 |
| 6 | 4 | 713 | 860 |
| 6 | 5 | 1269 | 1230 |
| 6 | 10 | 682 | 639 |
| 6 | 11 | 722 | 732 |
| 7 | 1 | 724 | 689 |
| 7 | 5 | 994 | 915 |
| 8 | 0 | 633 | 498 |
| 8 | 1 | 582 | 546 |
| 8 | 4 | 733 | 844 |
| ***** L = 13 ***** | | | |
| 0 | 2 | 1898 | 1865 |
| 0 | 4 | 1368 | 1396 |
| 0 | 6 | 590 | 523 |
| 0 | 8 | 2071 | 2068 |
| 0 | 10 | 592 | 683 |
| 0 | 12 | 872 | 883 |
| 0 | 14 | 839 | 961 |
| 1 | 1 | 1189 | 1098 |
| 1 | 2 | 512 | 535 |
| 1 | 3 | 1560 | 1553 |
| 1 | 7 | 1141 | 1106 |
| 1 | 9 | 1468 | 1404 |
| 1 | 12 | 577 | 465 |
| 1 | 13 | 976 | 1107 |
| 2 | 1 | 809 | 808 |
| 2 | 2 | 1239 | 1202 |
| 2 | 3 | 819 | 825 |
| 2 | 4 | 744 | 796 |
| 2 | 8 | 897 | 905 |
| 2 | 12 | 741 | 702 |
| 3 | 2 | 1186 | 1248 |
| 3 | 3 | 529 | 511 |
| 3 | 4 | 848 | 837 |
| 3 | 7 | 707 | 641 |
| 3 | 8 | 1134 | 1106 |
| 3 | 12 | 835 | 848 |
| 4 | 1 | 570 | 659 |
| 4 | 3 | 1248 | 1231 |
| 4 | 7 | 1055 | 1020 |
| 4 | 9 | 1016 | 1179 |
| 5 | 2 | 1035 | 1059 |
| 5 | 4 | 1080 | 1170 |
| 5 | 6 | 608 | 647 |
| 5 | 8 | 817 | 971 |
| 6 | 2 | 743 | 782 |
| 6 | 3 | 970 | 899 |
| 6 | 4 | 661 | 594 |
| 6 | 7 | 668 | 716 |
| 6 | 8 | 843 | 746 |
| 7 | 2 | 575 | 488 |
| 7 | 3 | 973 | 931 |
| ***** L = 14 ***** | | | |
| 0 | 0 | 1799 | 1769 |
| 0 | 2 | 588 | 461 |
| 0 | 4 | 899 | 899 |
| 0 | 6 | 967 | 1137 |
| 0 | 10 | 1070 | 1131 |
| 0 | 12 | 605 | 629 |
| 1 | 0 | 876 | 933 |
| 1 | 1 | 1174 | 1262 |
| 1 | 5 | 986 | 1077 |
| 1 | 7 | 879 | 921 |
| 1 | 9 | 748 | 712 |
| 1 | 11 | 894 | 939 |
| 2 | 0 | 1159 | 1127 |
| 2 | 1 | 983 | 982 |
| 2 | 4 | 782 | 881 |
| 2 | 5 | 596 | 727 |
| 2 | 6 | 779 | 822 |
| 2 | 9 | 691 | 672 |
| 2 | 10 | 724 | 798 |
| 2 | 11 | 671 | 768 |
| 3 | 0 | 1499 | 1517 |
| 3 | 4 | 867 | 897 |
| 3 | 6 | 1245 | 1186 |
| 3 | 10 | 1085 | 1069 |
| 3 | 12 | 729 | 626 |
| 4 | 1 | 900 | 918 |
| 4 | 3 | 659 | 513 |
| 4 | 5 | 1446 | 1339 |
| 4 | 7 | 623 | 689 |
| 4 | 9 | 672 | 532 |
| 4 | 11 | 1083 | 1023 |
| 5 | 0 | 1102 | 1093 |
| 5 | 2 | 635 | 478 |
| 5 | 3 | 559 | 341 |
| 5 | 4 | 1016 | 931 |
| 5 | 6 | 1217 | 1183 |
| 6 | 0 | 637 | 630 |
| 6 | 1 | 627 | 718 |
| 6 | 5 | 864 | 827 |
| 6 | 6 | 652 | 489 |
| 7 | 1 | 602 | 661 |
| ***** L = 15 ***** | | | |
| 0 | 2 | 1449 | 1489 |
| 0 | 4 | 926 | 972 |
| 0 | 8 | 1335 | 1357 |
| 0 | 12 | 708 | 756 |
| 1 | 1 | 840 | 818 |
| 1 | 3 | 1210 | 1216 |
| 1 | 7 | 725 | 681 |
| 1 | 9 | 711 | 745 |
| 1 | 12 | 601 | 447 |
| 2 | 1 | 810 | 820 |
| 2 | 2 | 738 | 682 |
| 2 | 7 | 755 | 662 |
| 2 | 8 | 893 | 809 |
| 3 | 2 | 1089 | 1093 |
| 3 | 4 | 691 | 754 |
| 3 | 8 | 855 | 1037 |
| 4 | 1 | 922 | 766 |
| 4 | 3 | 1240 | 1207 |
| 4 | 7 | 791 | 795 |
| 4 | 9 | 954 | 765 |
| 5 | 2 | 918 | 900 |
| 5 | 4 | 1053 | 904 |
| 5 | 6 | 659 | 501 |
| 5 | 7 | 594 | 373 |
| 6 | 3 | 644 | 661 |
| ***** L = 16 ***** | | | |
| 0 | 0 | 1517 | 1486 |
| 0 | 2 | 855 | 794 |
| 0 | 4 | 900 | 786 |
| 0 | 6 | 784 | 811 |
| 0 | 10 | 800 | 878 |
| 1 | 1 | 1165 | 1172 |
| 1 | 3 | 585 | 500 |
| 1 | 5 | 941 | 966 |
| 1 | 7 | 661 | 719 |
| 1 | 9 | 654 | 657 |
| 2 | 0 | 595 | 594 |
| 2 | 1 | 777 | 697 |
| 2 | 4 | 565 | 575 |
| 2 | 6 | 806 | 960 |
| 3 | 4 | 645 | 597 |
| 3 | 6 | 750 | 766 |
| 4 | 1 | 859 | 862 |
| 4 | 5 | 946 | 956 |
| 4 | 7 | 585 | 501 |
| 5 | 0 | 700 | 746 |
| 5 | 4 | 646 | 552 |
| ***** L = 17 ***** | | | |
| 0 | 2 | 1231 | 1261 |
| 0 | 4 | 575 | 571 |
| 0 | 6 | 709 | 754 |
| 1 | 1 | 692 | 689 |
| 1 | 3 | 939 | 975 |
| 1 | 7 | 803 | 702 |
| 2 | 3 | 647 | 536 |
| 2 | 7 | 574 | 548 |
| 3 | 2 | 1016 | 924 |
| 3 | 4 | 699 | 478 |
| 4 | 1 | 661 | 690 |
| 4 | 3 | 887 | 913 |
| ***** L = 18 ***** | | | |
| 0 | 0 | 1371 | 1327 |
| 0 | 2 | 628 | 657 |
| 1 | 1 | 764 | 775 |

typical carbon atom peak in earlier difference Fourier maps. Most of the higher peaks are in the region of the perchlorate group. Inspection of the final difference map showed no peak which could unambiguously be assigned to the hydrogen atom attached to the metal. Since the correct space group is noncentrosymmetric, this is not surprising.

The positional, thermal, and group parameters obtained from the last cycle of least-squares refinement are presented in Table I along with the associated standard deviations as estimated from the inverse matrix. The parameters of the ring carbon atoms and the perchlorate group oxygen atoms which may be derived from the data in Table I are presented in Table II, together with their thermal parameters as obtained from the last cycle of least-squares refinement. Final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III. Only the reflections used in the refinement are listed in this table. Of the 948 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, none had $|F_o^2 - F_c^2| > 3\sigma(F^2)$.

## Description and Discussion of Structure

The crystal structure of $[IrH(NO)(P(C_6H_5)_3)_3]$-$[ClO_4]$ consists of well-separated monomeric ions. The closest contact between the perchlorate oxygen atoms and the iridium atom is 4.31 Å. In Figure 1 a stereoscopic view of the unit cell of the compound is given, and in Figure 2 only the inner coordination about the iridium is shown. The root-mean-square amplitudes of vibration along the principal axes of thermal motion for the atoms which were treated anisotropically are given in Table IV. The directions of the principal

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

| Atom | Min | Intermed | Max |
|---|---|---|---|
| Ir | 0.170 (6) | 0.194 (5) | 0.207 (4) |
| P1 | 0.18 (2) | 0.19 (2) | 0.24 (2) |
| P2 | 0.15 (3) | 0.20 (1) | 0.25 (3) |
| P3 | 0.15 (2) | 0.20 (2) | 0.21 (2) |
| Cl | 0.26 (2) | 0.29 (2) | 0.33 (2) |
| N | 0.11 (9) | 0.29 (5) | 0.32 (5) |
| O1 | 0.28 (4) | 0.34 (4) | 0.37 (4) |

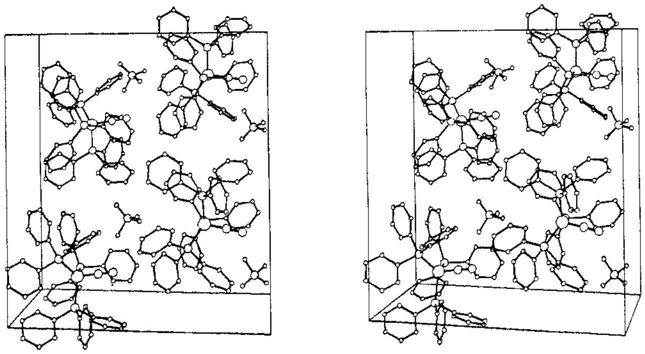

Figure 1.—A stereoscopic view of the contents of the unit cell of $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$. Hydrogen atoms on the phenyl groups are not shown.

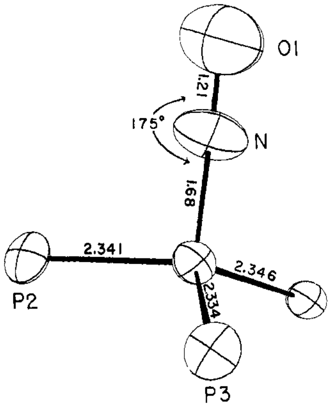

Figure 2.—The inner coordination sphere of the $IrH(NO)(P(C_6H_5)_3)_3^+$ ion. The 50% probability ellipsoids are shown. The H atom is not shown as it was not located in this study.

TABLE V

SELECTED BOND DISTANCES AND ANGLES

| Distance, Å | | | Angle, deg | | |
|---|---|---|---|---|---|
| Ir–P1 | 2.346 (9) | 2.340 (6) | Ir–N–O1 | 175.0 (3) | |
| Ir–P2 | 2.341 (8) | | P1–Ir–P2 | 118.4 (4) | |
| Ir–P3 | 2.334 (8) | | P1–Ir–P3 | 117.6 (4) | |
| Ir–N | 1.68 (3) | | P2–Ir–P3 | 110.4 (4) | |
| Ir–O1 | 2.89 (3) | | P1–Ir–N | 106 (1) | |
| | | | P2–Ir–N | 99 (1) | |
| N–O1 | 1.21 (3) | | P3–Ir–N | 103 (1) | |
| P1–P2 | 4.025 (13) | | | | |
| P1–P3 | 4.002 (13) | | | | |
| P2–P3 | 3.838 (12) | | | | |
| P1–N | 3.24 (3) | | Ir–P1–R1C1 | 115.9 (8) | |
| P2–N | 3.08 (4) | | Ir–P1–R2C1 | 109.1 (8) | |
| P3–N | 3.17 (3) | | Ir–P1–R3C1 | 118.6 (8) | |
| P1–R1C1 | 1.80 (2) | 1.83 (3) | Ir–P2–R4C1 | 114.1 (8) | |
| P1–R2C1 | 1.82 (2) | | Ir–P2–R5C1 | 108.5 (8) | |
| P1–R3C1 | 1.82 (2) | | Ir–P2–R6C1 | 121.5 (11) | |
| P2–R4C1 | 1.84 (2) | | Ir–P3–R7C1 | 109.7 (9) | |
| P2–R5C1 | 1.84 (2) | | Ir–P3–R8C1 | 116.2 (8) | |
| P2–R6C1 | 1.86 (3) | | Ir–P3–R9C1 | 116.8 (9) | |
| P3–R7C1 | 1.86 (3) | | R1C1–P1–R2C1 | 106 (1) | 104 (1) |
| P3–R8C1 | 1.80 (2) | | R1C1–P1–R3C1 | 102 (1) | |
| P3–R9C1 | 1.82 (2) | | R2C1–P1–R3C1 | 104 (1) | |
| Cl–O2 | 1.35 (3) | 1.44 (8) | R4C1–P2–R5C1 | 101 (1) | |
| Cl–O3 | 1.47 (3) | | R4C1–P2–R6C1 | 104 (1) | |
| Cl–O4 | 1.52 (3) | | R5C1–P2–R6C1 | 106 (1) | |
| Cl–O5 | 1.40 (4) | | R7C1–P3–R8C1 | 102 (1) | |
| | | | R7C1–P3–R9C1 | 105 (1) | |
| Ir···O2 | 6.15 (3) | | R8C1–P3–R9C1 | 106 (1) | |
| Ir···O3 | 6.44 (4) | | | | |
| Ir···O4 | 4.31 (3) | | | | |
| Ir···O5 | 6.42 (2) | | | | |

TABLE VI

SELECTED BOND DISTANCES AND ANGLES FOR SOME TRIGONAL-BIPYRAMIDAL AND TETRAHEDRAL TRIPHENYLPHOSPHINE COMPLEXES ($P(C_6H_5)_3 = L$)

| | $CoH(N_2)L_3$[a] | $RhH(CO)L_3$[b] | | $IrH(NO)L_3^+$[c] | | $Pt(CO)L_3$[d] | $Ir(NO)L_3$[e] |
|---|---|---|---|---|---|---|---|
| M–N(or C), Å | 1.81 (2) | 1.83 (3) | | 1.68 (3) | | 1.84 (2) | 1.67 (2) |
| M–P1, Å | 2.192 (15)[f] | 2.336 (8) | 2.322 (12) | 2.346 (9) | 2.340 (6) | 2.36 (1) | 2.31 (1) |
| M–P2, Å | | 2.316 (9) | | 2.341 (8) | | | |
| M–P3, Å | | 2.315 (8) | | 2.334 (8) | | | |
| P1–M–N(or C), deg | 98.0 (1.3)[f] | 94.8 (8) | 98.9 (5) | 106 (1) | 103 (3) | 113 (1) | 116.8 (5) |
| P2–M–N(or C), deg | | 104.0 (8) | | 99 (1) | | | |
| P3–M–N(or C), deg | | 97.8 (8) | | 103 (1) | | | |
| Av P–P, Å | 3.76 (7) | 3.98 (5) | | 3.96 (10) | | 3.76 (1) | 3.57 (1) |
| Av P–N(or C), Å | 3.03 (3) | 3.17 | | 3.16 (8) | | 3.51 (2) | 3.40 (2) |
| *d*,[g] Å | 0.30 | 0.36 | | 0.51 | | 0.92 | 1.04 |

[a] Reference 18. [b] Reference 16. [c] Present work. [d] V. G. Albano, G. M. B. Ricci, and P. L. Bellon, *Inorg. Chem.*, **8**, 2109 (1969). [e] V. G. Albano, P. L. Bellon, and M. Sansoni, personal communication. [f] Average for two independent molecules. [g] *d* is the distance from the metal to the P1P2P3 plane.

axes can be discerned at least approximately from Figure 2. Corrections of the bond lengths for the effects of thermal motion affect very little the differences among them.[17] The principal bond lengths and angles for the compound are given in Table V.

No symmetry is imposed on the molecule and the nitrogen and the three phosphorus atoms adopt an approximately tetrahedral geometry around the iridium atom. The hydrogen atom, which is coordinated to the metal, was not located in the structural determination; therefore its position cannot be assigned unambiguously. However, the close similarities of the geometries of the complexes $CoH(N_2)(P(C_6H_5)_3)_3$[18] and $RhH(CO)(P(C_6H_5)_3)_3$[16] and $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ (see Table VI) strongly suggest that for the nitrosyl complex the hydride ligand occupies the axial position of a distorted trigonal bipyramid trans to the nitrosyl group and the three phosphorus atoms occupy the equatorial positions. The Ir–N–O angle is 175 (3)° and the Ir–N bond length is 1.68 (3) Å. Metal–nitrogen bond lengths for nitrosyl complexes which have been formulated as $NO^+$ complexes have Ir–N bond lengths in the range 1.57–1.77 Å and metal–N–O bond angles in the range 160–180° (see Table VII and ref 3, Table VI), whereas those that have been formulated as $NO^-$ complexes generally have longer bond lengths of 1.89–1.97 Å and metal–N–O bond angles of approximately 120° (see Table VII). Therefore $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ is best formulated as an $NO^+$ complex of iridium(I). The trigonal-bipyramidal geometry of the ligands around the metal is also consistent with this formulation because all five-coordinate iridium(I) and rhodium(I) complexes whose structures have been determined have trigonal-bipyramidal ge-

---

(17) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

(18) B. R. Davis, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, **8**, 2719 (1969).

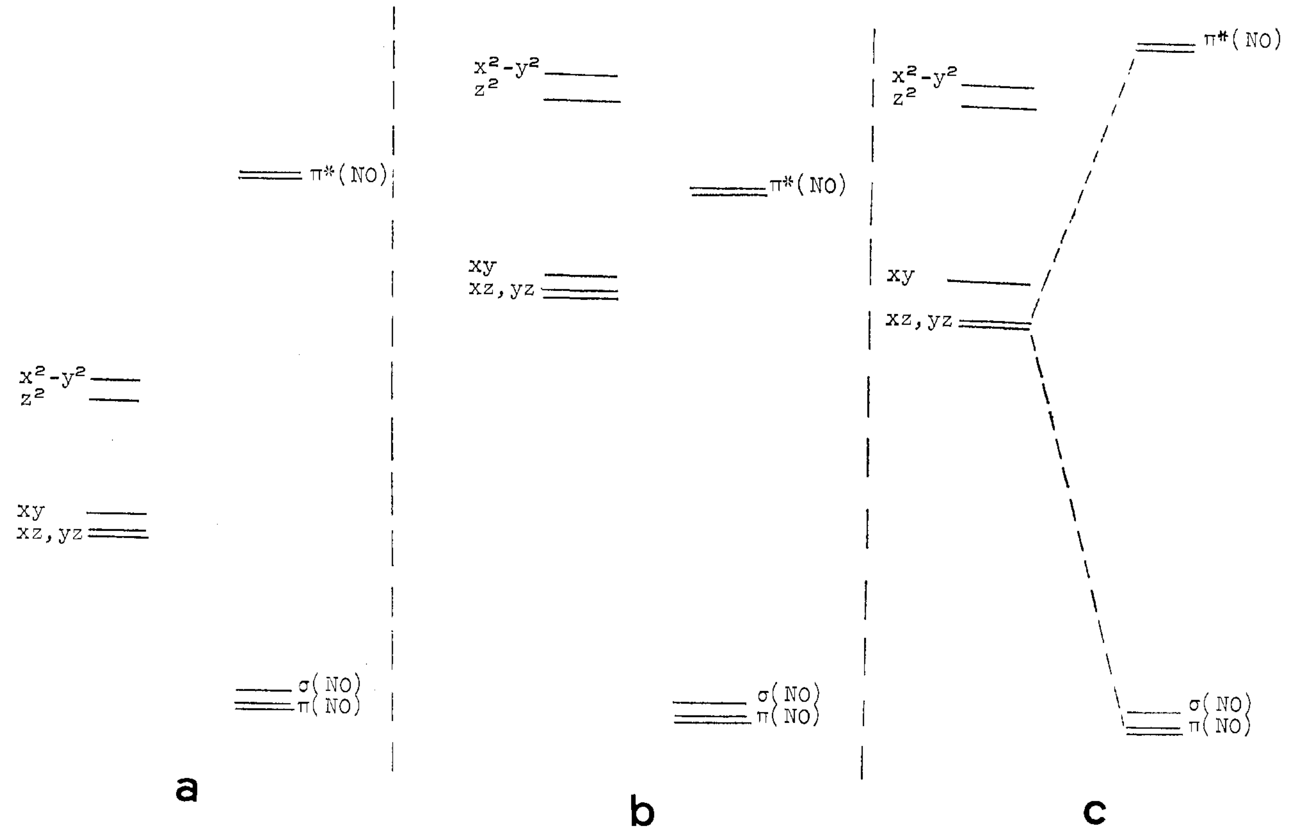

Figure 3.—Qualitative molecular orbital schemes for a complex of the type $M(NO)L_4$ of $C_{4v}$ symmetry, with the metal in different oxidation states and with different degrees of metal–nitrosyl π bonding. (a) A molecular orbital scheme for the complex when the metal is in a high oxidation state and the degree of metal–nitrosyl π bonding is minimal. (b) The metal is in a lower oxidation state and therefore the energies of the metal d orbitals are higher, but the degree of metal–nitrosyl π bonding is still minimal. (c) The effect of extensive π bonding between the metal and the nitrosyl ligand.

TABLE VII

SELECTED METAL–NITROGEN BOND LENGTHS, METAL–NITROGEN–OXYGEN BOND ANGLES, AND INFRARED NITROSYL STRETCHING FREQUENCIES ($L = P(C_6H_5)_3$; en = ETHYLENEDIAMINE)

| Compd | M–N, Å | M–N–O, deg | ν(NO), cm⁻¹ | Formulation |
|---|---|---|---|---|
| $[RuCl(NO)_2L_2][PF_6]$ | 1.74 (2)[a] | 180 (2) | 1845[a] | $NO^+$ |
| $Ir_2O(NO)_2L_2$ | 1.76 (2)[b] | 177 (2) | 1758–1735[b] | $NO^+$ |
| $[IrH(NO)L_3][ClO_4]$ | 1.68 (3)[c] | 175 (3) | 1780[k] | $NO^+$ |
| $Ir(NO)L_3$ | 1.67 (2)[d] | 180 | 1600[k] | $NO^+$ |
| $[IrI(NO)(CO)L_2][BF_4]$ | 1.89 (3)[e] | 125 (3) | 1720[e] | $NO^-$ |
| $[RuCl(NO)_2L_2][PF_6]$ | 1.86 (2)[a] | 136 (1) | 1687[a] | $NO^-$ |
| $[IrCl(NO)(CO)L_2][BF_4]$ | 1.97 (1)[f] | 124 (1) | 1680[f] | $NO^-$ |
| $[CoCl(NO)(en)_2][ClO_4]$ | 1.81 (1)[g] | 121 (1) | 1611[l] | $NO^-$ |
| $[Co(NO)(NH_3)_5]Cl_2$ | 1.87 (1)[h] | 119 (1) | 1610[m] | $NO^-$ |
| $IrCl_2(NO)L_2$ | 1.94 (2)[i] | 123 (2) | 1560[k] | $NO^-$ |
| $IrI(CH_3)(NO)L_2$ | 1.91 (2)[j] | 120 (2) | 1525[k] | $NO^-$ |

[a] C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92,** 4760 (1970). [b] P. Carty, A. Walker, M. Mathew, and G. J. Palenik, *Chem. Commun.*, 1374 (1969). [c] Present work. [d] V. G. Albano, P. L. Bellon, and M. Sansoni, personal communication. [e] Reference 4. [f] References 2 and 3. [g] D. A. Snyder and D. L. Weaver, *Chem. Commun.*, 1425 (1969). [h] C. S. Pratt, B. Coyle, and J. A. Ibers, *J. Chem. Soc.*, in press. [i] Reference 1. [j] Reference 5. [k] Reference 6. [l] R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4,** 1334 (1965). [m] E. E. Mercer, W. A. McAllister, and J. R. Durig, *ibid.*, **6,** 1816 (1967).

ometries. The geometry and resulting formulation of the complex $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ as an $NO^+$ complex of iridium(I) is surprising because the closely related complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ ($X = Cl, I$) and $IrXY(NO)(P(C_6H_5)_3)_2$ ($X = Y = Cl$; $X = CH_3$, $Y = I$) have square-pyramidal geometries and Ir–N–O bond angles of approximately 120° and consequently have been formulated as $NO^-$ complexes of iridium(III).[1–5]

This marked difference in geometries is reminiscent of the large changes in bond angle associated with the reduction of $NO_2^+$, which is linear, to $NO_2^-$, which has a bond angle of approximately 120°. The former may naively be considered as an $NO^+$ complex of the oxygen atom and the latter as an $NO^-$ complex of oxygen. This difference in geometries may be rationalized by Walsh's rules.[19] The two electrons which are added to $NO_2^+$ to form $NO_2^-$ must be placed in a doubly degenerate orbital of $\pi_u$ symmetry, which results in a triplet ground state. Walsh has shown that for such an electronic configuration an angular distortion which removes the degeneracy leads to a net gain in energy.[19]

The transformation from $NO_2^+$ to $NO_2^-$ must be accompanied by the oxidation of an external reducing agent. However, if the $NO^+$ moiety is attached to a transition metal ($M^N$, where $N$ is the oxidation state), reduction to $NO^-$ may instead be accompanied by a change in oxidation state of the metal of +2, to give the species $M^{N+2}\text{–}NO^-$. The form $M^N\text{–}NO^+$ will be more stable as long as the metal d orbitals are more stable than the $\pi^*(NO)$ orbitals (see Figure 3a). This will be the case when the metal is in a high oxidation state. For this class of complexes the M–N–O bond would be expected to be linear because the $\pi^*(NO)$ orbitals remain degenerate.

If the oxidation state of the metal is lower, the metal d orbitals and the $\pi^*(NO)$ orbitals are likely to have

---

(19) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

comparable energies (see ref 1 for a more detailed discussion of this point). For example, for a $d^8$ complex of $C_{4v}$ symmetry with the metal in a low oxidation state one might have the situation shown in Figure 3b, where the doubly degenerate $\pi^*(NO)$ orbital is of lower energy than the metal $d_{z^2}$ orbital, and consequently it is preferentially occupied. Because of this electron transfer the species may now be formulated as $M^{N+2}$–$NO^-$. The presence of two electrons in the doubly degenerate $\pi^*(NO)$ orbital is exactly analogous to the $NO_2^-$ example discussed above, which suggests that a distortion from linearity will result to give a nonlinear $M^{N+2}$–$NO^-$ species. This is in agreement with the results for the $NO^-$ complexes studied in this and other laboratories (see Table VII). This model also suggests that the electron transfer to give the $NO^-$ complex might also have a dramatic effect on the overall geometry around the metal if different geometries are preferred for the $M(N)$ and $M(N + 2)$ oxidation states. As pointed out previously[1] five-coordinate complexes of the $d^8$ platinum metals generally adopt trigonal-bipyramidal geometries and the $d^6$ complexes usually adopt square-pyramidal geometries. This is in accord with the result that the $Ir^I$–$NO^+$ complex $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ has a trigonal-bipyramidal geometry and the $Ir^{III}$–$NO^-$ complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl, I)[2-4] and $IrXY(NO)(P(C_6H_5)_3)_2$ (X = Y = Cl;[1] and X = $CH_3$, Y = I[5]) have square-pyramidal geometries and nonlinear metal–nitrogen–oxygen bond angles.

In contrast to the above effect, the oxidation state of the metal will also influence the energies of the $\pi^*(NO)$ orbitals through $\pi$-bonding effects. Overlap between metal orbitals of $\pi$ symmetry and the $\pi^*(NO)$ orbitals will have the effect of raising the energies of the latter orbitals (Figure 3c). The presence of two opposing effects makes it impossible to predict the exact situation which will favor formation of $NO^-$ complexes, yet one can say that $NO^-$ complexes are unlikely to be found for high oxidation states because bonding effects will be minimal and also the metal d orbitals will be lower in energy than the $\pi^*(NO)$ orbitals.

Attempts at correlation of metal oxidation states with formation of $NO^+$ and $NO^-$ complexes are fraught with difficulty because the formal oxidation state of the metal in $NO^-$ complexes represents the oxidation state of the metal after electron transfer, *i.e.*, the oxidation state on the right-hand side of the equation

$$M^N\text{–}NO^+ \rightleftarrows M^{N+2}\text{–}NO^-$$

However, if we are interested in the factors influencing the relative stabilities of the species on the right- and left-hand sides of the equation, all the compounds must be compared on an equal basis, that is, either all as $NO^+$ or all as $NO^-$. Alternatively, no assumptions need be made about the bonding and a comparison of the oxidation states could be made on the basis that nitric oxide is a neutral ligand $NO\cdot$.

If such a consistent scheme is used for assigning oxidation states, it becomes apparent that coordination as $NO^+$ is favored for high oxidation states, *e.g.*, $Na_2[Ru(OH)(NO_2)_4(NO)]$ ($Ru^{III}$–$NO\cdot$),[20] and low oxidation states, *e.g.*, $Ir(NO)(P(C_6H_5)_3)_3$,[21] $Mn(NO)(CO)_4$,[22] and $Co(NO)(CO)_3$[23] (all $M^0$–$NO\cdot$). However coordination as $NO^-$ appears to be favored in intermediate oxidation states, for example, $IrCl_2(NO)(P(C_6H_5)_3)_2$ ($Ir^{II}$–$NO\cdot$).[1] Presumably, in low oxidation states the degree of interaction between the metal $\pi$ and the $\pi^*(NO)$ orbitals is sufficiently large to raise the energy of the $\pi^*(NO)$ orbitals to a position above that of the metal d orbitals.

Similar arguments can be made to rationalize the observed geometries of the $NO^-$ complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl, I) and $IrXY(NO)(P(C_6H_5)_3)_2$ (X = Y = Cl; X = $CH_3$, Y = I) and the trigonal-bipyramidal $NO^+$ complex $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$. In the latter, the nonnitrosyl ligands attached to the metal all have low electronegativities and hence there is more electron density on the iridium atom than in the other compounds; thus there is increased interaction between the metal and the $\pi^*(NO)$ orbitals, and the energies of the $\pi^*(NO)$ orbitals will be increased as in Figure 3c. If these orbital energies are raised above those of the metal d orbitals by this effect, electron transfer will no longer be energetically favorable and the complex will have the electronic configuration $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^2(d_{x^2-y^2})^0(\pi^*(NO))^0$, formally $Ir^I$–$NO^+$. This contrasts with electron configuration proposed for the other iridium complexes mentioned above, $(d_{xz})^2(d_{yz})^2(d_{xy})^2(\pi^*(NO))^2(d_{z^2})^0(d_{x^2-y^2})^0$, formally $Ir^{III}$–$NO^-$.

Table VI compares some important bond lengths and angles for a series of closely related complexes of the type $MX(P(C_6H_5)_3)_3$ and $MHX(P(C_6H_5)_3)_3$ (X = CO, $NO^+$; M = Rh(I), Pt(0), Co(I), Ir(I), Ir(−I)). A comparison of the data for $RhH(CO)(P(C_6H_5)_3)_3$[16] and $Pt(CO)(P(C_6H_5)_3)_3$[24] *vs.* $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ and $Ir(NO)(P(C_6H_5)_3)_3$[21] indicates that the hydride ligand definitely plays a significant role in determining the final geometries of the complexes. These comparisons are particularly pertinent because the M–X distances are equivalent and therefore the nonbonded repulsions between the axial and equatorial ligands are likely to be the same in the two sets of compounds. Although there are significant distortions from the ideal trigonal-bipyramidal geometry for the hydrido complexes, the P–M–X angles are still 14° smaller than the corresponding angles for the four-coordinate complexes. This behavior contrasts with the observation that in the complex $RhH(P(C_6H_5)_3)_4$ the phosphorus atoms are arranged tetrahedrally around the metal atom and the stereochemical influence of the hydride ligand appears to be minimal.[25]

The distance of the iridium atom from the plane made by the three phosphorus atoms may be taken as a measure of the distortion from the ideal trigonal-bipyramidal geometry. Of course this distance is zero for the ideal trigonal-bipyramidal geometry. The distortions from the ideal do not appear to result from nonbonded repulsions between the axial ligand and

---

[20] S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, **27**, 307 (1965).

[21] V. G. Albano, P. L. Bellon, and M. Sansoni, personal communication.

[22] B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).

[23] L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1967).

[24] V. G. Albano, G. M. B. Ricci, and P. L. Bellon, *Inorg. Chem.*, **8**, 2109 (1969).

[25] R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

the three ligands in the equatorial plane, because the P–X distance is smallest for the complex which shows the smallest distortion, *i.e.*, $CoH(N_2)(P(C_6H_5)_3)_3$. In cases where it has been postulated that nonbonded repulsions are playing a significant role in determining the final geometry of tertiary phosphine complexes, the X–P distances for all compounds have remained almost constant.[26] Also from considerations of nonbonded repulsions it is difficult to understand why the four-coordinate complexes have X–M–P angles greater than the ideal tetrahedral values although the P–X nonbonded contacts are relatively large (3.4–3.5 Å). We think that the geometries of these complexes may be rationalized by a consideration of the electron-pair repulsions between the M–X and M–P bonds.[27] All the ligands X are capable of forming bonds to the metal with some double-bond character. A consideration of the sum of the covalent radii[28] for the three five-coordinate complexes in Table VI indicates that the ability of X to form multiple bonds with the metal is in the order $NO^+ > CO > N_2$. The electron density in the M–X bond will also follow this order and will be greatest for the nitrosyl complex and least for the nitrogen complex. If electron repulsions are important, the degree of distortion from the ideal will take the following order: $IrH(NO)(P(C_6H_5)_3)_3^+ > RhH(CO)(P(C_6H_5)_3)_3 > CoH(N_2)(P(C_6H_5)_3)_3$, which is the observed order. For five-coordinate complexes the distortions will be limited by the steric requirements of the hydride ligand and would be expected to be less than the distortions in the corresponding four-coordinate complexes, which have approximately the same degree of multiple-bond character as evidenced by the very similar M–C and M–N distances for the carbonyl and nitrosyl complexes. For the four-coordinate complexes the distortions are limited only by the steric requirements of the phenyl rings and this results in X–M–P bond angles greater than the ideal tetrahedral values. Table VI also shows that the degree of distortion is greater for $Ir(NO)(P(C_6H_5)_3)_3$ than for $Pt(CO)(P(C_6H_5)_3)_3$ as one would expect from a consideration of electron-pair repulsions.

We also wish to emphasize the inadequacies of using the $\nu$(NO) stretching frequency to diagnose the mode of coordination of the nitrosyl ligand. Table VII shows $\nu$(NO) for some nitrosyl complexes whose structures have been determined recently. The $NO^+$ complexes have $\nu$(NO) in the range 1600–1845 $cm^{-1}$ and for the $NO^-$ complexes $\nu$(NO) is in the range 1525–1720 $cm^{-1}$. The large area of overlap precludes any formulation based solely on $\nu$(NO) in the region 1600–1720 $cm^{-1}$ and frequencies close to these ought also to be treated with caution. Also no direct correlation between $\nu$(NO) and the metal–nitrogen bond length exists.

**Acknowledgment.**—We wish to thank the National Institutes of Health for support of this work.

---

[26] D. Bright and J. A. Ibers, *Inorg. Chem.*, **8**, 709 (1969).

[27] R. J. Gillespie and R. S. Nyholm, *Progr. Stereochem.*, **2**, 261 (1958).

[28] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

---

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

# Conformational Effects of Intermolecular Interactions. The Structure of Tris(ethylenediamine)cobalt(III) Monohydrogen Phosphate Nonahydrate

BY EILEEN N. DUESLER AND KENNETH N. RAYMOND*

*Received December 21, 1970*

The crystal and molecular structure of racemic tris(ethylenediamine)cobalt(III) monohydrogen phosphate nonahydrate, $[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$, has been determined by three-dimensional X-ray methods. The salt crystallizes in the orthorhombic space group *Pnma* with four formula units in a cell of dimensions $a = 15.616$ (5), $b = 27.514$ (8), and $c = 8.719$ (3) Å. The calculated density of 1.65 g/cm³ compares well with the observed density of 1.64 g/cm³. The structure has been refined by full-matrix least-squares methods for 2423 independent reflections to a final agreement factor of 5.0%. The structure is composed of waters of hydration and $Co(en)_3^{3+}$ and $HPO_4^{2-}$ ions linked by hydrogen bonds. One of the $HPO_4^{2-}$ units is on a crystallographic mirror plane and relates an enantiomorphous pair of $Co(en)_3^{3+}$ cations. This biphosphate is positioned approximately on the molecular threefold axes of both cations, forms hydrogen bonds with both cations, and locks them in the $\Lambda\delta\delta\delta$ and $\Delta\lambda\lambda\lambda$ conformations, respectively.

## Introduction

The absolute configuration[1] and conformational analysis[2] of the $Co(en)_3^{3+}$ cation have been the subjects of considerable interest and study, and these compounds have been used as a testing ground for models relating optical rotatory strength with structure.[3,4] One of the most curious observations in this area is that the circular dichroism spectrum of aqueous solutions of $Co(en)_3^{3+}$ changes dramatically when an excess of phosphate ion is added.[5] An explanation[5-7] was offered for this phenomenon which hypothesized that an ion pair is formed which strongly affects the charge-transfer and circular dichroism spectra. Hydrogen-bonding effects have previously been found dramatically to alter the conformations of several tris-ethylenediamine complex cat-

---

[1] K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **30**, 158 (1957).

[2] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[3] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

[4] W. Moffitt, *ibid.*, **25**, 1189 (1956).

[5] S. F. Mason and B. J. Norman, *Proc. Chem. Soc., London*, 339 (1964).

[6] H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).

[7] L. R. Froebe and B. E. Douglas, *ibid.*, **9**, 1573 (1970).