that the systems would differ considerably. Lynds, *et al.*,[11] presented two equations to describe the decrease in the lattice parameter as the oxide content of the lattice increases: one for the composition range UO_2–$UO_{2.125}$ and another for the range $UO_{2.17}$–$UO_{2.25}$. The first equation characterizes the behavior of a nonstoichiometric UO_2 phase while the second characterizes that of a U_4O_9 phase ($UO_{2.25}$). The first of these has a clear counterpart in the samarium fluoride system but the second does not, probably because a clearly defined $SmF_{2.25}$ analog could not be found. However, a single-crystal study by Belbeoch, *et al.*,[12] has demonstrated that the unit cell of $UO_{2.25}$ contains 64 nominally fluorite unit cells arranged in a $4 \times 4 \times 4$ array. The superstructure observed in the latter half of the cubic–tetragonal two-phase region and assigned to the tetragonal unit cell may, in fact, correspond to a similar type of cell and an $SmF_{2.25}$ phase may exist. The concurrence of a phase boundary at $SmF_{2.16}$ and $UO_{2.17}$ provides some support for the existence of a phase at $SmF_{2.25}$.

Another phase in the uranium–oxygen system, $UO_{2.33}$ (U_6O_{14}), a member of a homologous series (U_nO_{2n+2}) reported for this system by Makarov,[10] has a similar analog in the samarium system, $SmF_{2.35}$. Hoekstra, *et al.*,[13] have reported that this uranium phase possesses body-centered tetragonal symmetry with $a = 3.78$ and $c = 5.55$ Å. As in the samarium phase, the a parameter is less than half the face diagonal of a cube with edge c. A modification of this tetragonal cell in which $a = 3.84$ and $c = 5.40$ Å has been observed for only the uranium–oxygen system.

The next phase in the homologous series, $UO_{2.40}$ (U_5O_{12}), has been reported to be tetragonal with $a = 5.364$ and $c = 5.531$ Å. The phase $SmF_{2.41}$, which has been indexed on a rhombohedral lattice, seems to be related to this uranium analog.

The samarium analog of $UO_{2.5}$ (U_4O_{10}) may correspond to $SmF_{2.46}$, but the relationship is not so well defined. The uranium compound has been examined by single-crystal techniques and has been found to be orthorhombic.[10] It seems apparent that while many of the same stoichiometries are involved, the lattice modifications are different for the two systems. The uranium system displays at least one more phase, with several crystal modifications, before the lattice collapses to that of UO_3, and thus appears to be more complicated at the anion-rich end of the nonstoichiometric region. This complexity probably results from the different charges and sizes of the ions.

It is apparent from the above discussion that the nonstoichiometry displayed by these two systems is the result of similar modifications of the fluorite lattice. The present investigation has been unable to establish the nature of these changes and has indicated that single-crystal studies must be undertaken to clarify some of the observations.

Acknowledgment.—The support of the U. S. Atomic Energy Commission (AT(11-1)-716) is gratefully acknowledged.

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The Crystal and Molecular Structure of Dinitrosylbis(triphenylphosphine)iridium Perchlorate, $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$

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The structure of dinitrosylbis(triphenylphosphine)iridium perchlorate, $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group C_{2h}^6-C2/c of the monoclinic system with four molecules in a unit cell of dimensions $a = 17.090$ (16) Å, $b = 12.413$ (13) Å, $c = 17.165$ (17) Å, and $\beta = 108.02$ (11)°. The observed and calculated densities are 1.69 ($\pm$0.02) and 1.68 g/cm³, respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.043 for the 1597 independent reflections having $F^2 > 3\sigma(F^2)$. The crystal structure consists of well-separated, discrete, monomeric ions. The coordination geometry around the iridium atom is only approximately tetrahedral; the N–Ir–N angle, 154.2 (7)°, is much larger than expected. Possible reasons for this distortion are discussed. The iridium–nitrogen–oxygen bond angle of 164 (1)° deviates considerably from linearity. The perchlorate anion is disordered about two positions and has been refined as a rigid group, with normal tetrahedral angles of 109° 28′ and chlorine–oxygen bond lengths of 1.43 Å.

Introduction

Crystal structure studies of $[IrX(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or I)[1-3] showed that in each compound the metal–nitrosyl geometry was very different from that previously observed in reliable structural studies of transition metal–nitrosyl complexes. Whereas the usual transition metal–nitrosyl geometry involves a short metal–nitrogen bond and a linear or nearly linear metal–nitrogen–oxygen bond angle,

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the structural studies of the iridium systems showed that the geometry involved a long metal–nitrogen bond and a metal–nitrogen–oxygen bond angle of approximately 120°. These studies led to the suggestion[1] that while in the usual transition metal–nitrosyl complexes the nitrosyl ligand is acting as a Lewis base (NO^+), in the iridium systems it is acting as a Lewis acid (NO^-). We were thus prompted to examine other nitrosyl complexes where the nitrosyl ligand might be acting as a Lewis acid.

Angoletta, Malatesta, and Caglio[4,5] isolated $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ by treating an ethanolic solution of $[IrH_2(P(C_6H_5)_3)_2][ClO_4]$ with nitric oxide. On the basis of its infrared spectrum, the complex was formulated as containing iridium(−I), with the nitrosyls coordinated as "NO^+." Such a d^{10} complex would be expected to be tetrahedral. However, the reactions of this complex are not completely consistent with this formulation. For example, the complex reacts with lithium halides to give the neutral five-coordinate compounds $IrX(NO)_2(P(C_6H_5)_3)_2$ (X = Cl, Br, or I), which have two electrons greater than that predicted by the inert-gas rule. In such a complex the additional electrons probably reside on the amphoteric nitrosyl ligands rather than in antibonding metal–ligand σ orbitals. No similar reactions have been reported for the analogous complexes $Pt(CO)_x(P(C_6H_5)_3)_{4-x}$ ($x = 0$–2).[6] This unusual reaction may be rationalized in two ways. Either the starting complex is not iridium(−I) but iridium(I), or nucleophilic attack by the halide ions causes internal electron transfer to occur from one of the nitrosyl σ-bonding molecular orbitals to antibonding orbitals localized mainly on the nitrosyls thus leaving an empty σ-bonding orbital available for the lone pair of electrons of the halide ion. The iridium(I) ion may formally be written as $Ir(NO^+)(NO^-)(P(C_6H_5)_3)_2{}^+$, although this is an oversimplification and the electrons may actually be delocalized over both nitrosyls. Such an iridium(I) ion would be expected to be square planar. The present structural study of $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ was undertaken to gain an insight into the oxidation state of the iridium atom and perhaps to understand the unusual reactions of this complex.

Collection and Reduction of Intensity Data

Violet, well-formed crystals of $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ were prepared by the method of Angoletta and Caglio[4] and were characterized by their melting point, infrared spectrum, and elemental analysis. On the basis of Weissenberg and precession photography of the $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, and $2kl$ nets using Mo Kα and Cu Kα radiation, it was established that the crystals belong to the monoclinic system. The observed extinctions $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ suggested the space groups $C_{2h}{}^6$-C2/c or $C_s{}^4$-Cc. On the basis of optical goniometry, the crystal faces were identified as belonging to the forms $\{\bar{1}11\}$ and $\{100\}$. The lattice constants at 23°, which were determined from a least-squares refinement of the setting angles of 21 strong X-ray reflections which had been centered on a Picker four-circle automatic diffractometer[7] using Mo Kα_1 radiation (λ 0.70930 Å), are a = 17.090 (16) Å, b = 12.413 (13) Å, c = 17.165 (17) Å, and β = 108.02 (11)°. The density calculated for four formula weights per unit cell is 1.68 g/cm^3, which agrees well with that of 1.69 (±0.02) g/cm^3 measured by suspending crystals in a mixture of diiodomethane and carbon tetrachloride. With four formula weights per unit cell either a twofold axis or a center of symmetry is imposed on the ions in the space group C2/c but no symmetry is imposed in the noncentric space group Cc.

The mosaicity of the crystal was examined by means of the narrow source, open counter, ω-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 0.53 × 0.063 × 0.063 mm. The crystal was mounted on the diffractometer with the needle direction ([101] zone axis) almost coincident with the diffractometer spindle axis.

For data collection Mo Kα radiation was used and the diffracted beams were filtered through 3.0 mils of zirconium foil. The intensities were measured by the θ–2θ technique at a takeoff angle of 1.3°. At this angle the intensity of a reflection was about 80% of the maximum value as a function of takeoff angle. A receiving counter aperture 4 × 4 mm was used and was positioned 35 cm from the crystal. A nonsymmetric scan range in 2θ was used, from −0.5 to +1.0 from the Kα_1 peak. Stationary counter–stationary crystal background counts of 10 sec were measured at each end of the scan. 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 Kα peak.

The unique data set having $2\theta < 40°$ was gathered; the intensities of a total of 1882 independent reflections were recorded. The intensities of five standard reflections, measured after every 200 reflections, remained essentially constant throughout the run, showing only the deviations of less than ±1%. There were very few reflections above background at values of $2\theta > 40°$.

All data processing was carried out as previously described.[7] The value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Of the 1882 reflections, 144 had

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(4) M. Angoletta and G. Caglio, *Gazz. Chim. Ital.*, **93**, 1584 (1963); L. Malatesta, M. Angoletta, and G. Caglio, *Angew. Chem.*, **75**, 1103 (1963).

(5) M. Angoletta, *Gazz. Chim. Ital.*, **93**, 1591 (1963).

(6) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(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.

intensities which were less than their standard deviations. The linear absorption coefficient, μ, for this compound using Mo Kα radiation is 43.30 cm^{-1}. For this crystal trial calculations showed that the transmission coefficients ranged only from 0.78 to 0.75 and therefore no absorption correction was made.

Solution and Refinement

The space group was assumed to be C2/c and the iridium and phosphorus atoms were located from a three-dimensional, origin-removed, sharpened Patterson function.[9] The position of the iridium at 0, y, $^1/_4$ requires that twofold symmetry be imposed on the cation. A least-squares refinement on F was computed and the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 4F_o^2/\sigma^2(F_o^2)$, and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. In all calculations of F_c, the atomic scattering factors of iridium were taken from Cromer and Waber,[10] and those for hydrogen, from Stewart, Davidson, and Simpson.[11] Scattering factors for all other atoms were taken from the usual tabulation.[12] The effects of anomalous dispersion were included in the calculations of F_c.[13] The values of $\Delta f'$ and $\Delta f''$ were taken from Cromer's calculations.[14] Only the 1597 reflections which had intensities greater than three times their standard deviations were included in the structural refinement. The iridium and phosphorus atoms were assigned isotropic thermal parameters and one cycle of least-squares refinement gave the agreement factors $R_1 = 0.229$ and $R_2 = 0.302$, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

A subsequent difference Fourier synthesis led to positions of all the nonhydrogen atoms of the cation and to that of the perchlorate chlorine atom. The parameters obtained from this map were refined by least-squares methods. The nonphenyl atoms were refined with isotropic thermal parameters; the phenyl rings were treated as rigid groups and restricted to their known geometry (D_{6h} symmetry, d(C–C) = 1.390 Å). The variable parameters for the rings included an overall isotropic thermal parameter, the coordinates of the ring center, and three orientation angles, which have been defined previously.[15-17] Two cycles of refinement gave the agreement factors $R_1 = 0.083$ and $R_2 = 0.109$. Examination of another difference Fourier map revealed 14 of the 15 phenyl hydrogen atoms. This in part justifies our original assumption that the compound belongs to the space group C2/c rather than Cc.

Although the perchlorate group could possess a crystallographic twofold axis and be ordered, examination of the difference Fourier map revealed that this was not so but rather that the perchlorate group was disordered over two sites related by the twofold axis. Three of the four independent half-oxygen atoms displayed peak heights of 2.2–2.8 e$^-$/Å^3 while the fourth half-oxygen atom had a peak height of 1.3 e$^-$/Å^3. The geometry, derived from the interpolated positions of the peak centers, was a reasonable one for a perchlorate group.

At this point the phenyl proton contributions to the structure factors were included as a fixed contribution (d(C–H) = 1.08 Å and the isotropic group thermal parameters were made equal to the corresponding carbon group thermal parameters). In a further refinement cycle all nongroup atoms, except for the perchlorate oxygens, were allowed to vibrate anisotropically and individual, variable isotropic thermal parameters were assigned to each of the ring carbon atoms. Two cycles of refinement yielded agreement factors of $R_1 = 0.040$ and $R_2 = 0.049$ for the 90 variables and 1597 observations. However, this treatment yielded an unsatisfactory geometry for the perchlorate group. Although the O–Cl–O bond angles were within the tolerable range of 99–121°, three of the Cl–O bond lengths were too long (1.50–1.56 Å) and the fourth was too short (1.20 Å). Such a disparity in bond lengths could be the result of disorder of the chlorine atom about the twofold axis. In the final round of calculations the perchlorate oxygen atoms were treated as a group with Cl–O distances of 1.43 Å and O–Cl–O angles of 109° 28′ and were assigned individual isotropic temperature factors. The origin of the O_4 group was restricted to the twofold axis. After three cycles of least-squares refinement, the agreement factors were $R_1 = 0.043$ and $R_2 = 0.052$ (with 82 variables). The final parameters for the cation are essentially the same as those calculated for the first model. A final difference Fourier map revealed two peaks of heights 1.2 and 1.0 e$^-$/Å^3 at 1.5 and 1.6 Å from the chlorine atom. Presumably our model for the disorder is not completely satisfactory.

Two other models for the disorder were examined, but neither was as satisfactory as the one above. One model treated the perchlorate oxygens as a group not restricted to the twofold axis and the chlorine atom was treated as an individual atom with anisotropic temperature factors. This calculation led to agreement factors similar to those above but gave unreasonable Cl–O bond lengths as the centroid of the group did not coincide with the position of the chlorine atom. The other model treated all five of the ClO_4 atoms as a group, and gave similar agreement factors. However a difference Fourier map revealed a considerable amount of electron density around the chlorine atom, probably because the chlorine atom was not refined anisotropically.

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(9) In addition to various local programs, the programs used in the refinement of this structure were local modifications of Hamilton's GONO9 absorption correction program, Busing and Levy's ORFFE function and error 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.

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

(12) J. A. Ibers in "International Tables of X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, Table 3.3.1.A.

(13) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

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

(15) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(16) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

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TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0	0.03051 (5)[b]	1/4	0.00300 (3)	0.00495 (5)	0.00320 (3)	0	0.00035 (2)	0
Cl	1/2	0.1154 (5)	1/4	0.0061 (3)	0.0158 (6)	0.0036 (2)	0	0.0016 (2)	0
P	0.0994 (2)	0.1299 (2)	0.3480 (2)	0.0028 (1)	0.0051 (2)	0.0028 (1)	0.0000 (1)	0.0010 (1)	−0.0002 (1)
N	0.0552 (6)	−0.0014 (8)	0.1811 (7)	0.0041 (5)	0.0097 (10)	0.0045 (5)	0.0011 (5)	0.0000 (4)	−0.0019 (5)
O	0.0923 (7)	0.0046 (10)	0.1314 (7)	0.0064 (5)	0.0231 (15)	0.0059 (5)	0.0022 (7)	0.0024 (5)	−0.0038 (7)

Group	x_c[c]	y_c	z_c	δ	ϵ	η
R1	0.2065 (3)	0.2827 (4)	0.2700 (3)	0.407 (5)	−2.660 (5)	−0.765 (5)
R2	0.2279 (3)	−0.0243 (4)	0.4746 (3)	2.294 (4)	−2.958 (5)	2.597 (5)
R3	0.0266 (3)	0.2723 (4)	0.4648 (3)	0.942 (6)	2.434 (4)	1.333 (6)
O4[d]	1/2	0.1157 (13)	1/4	−2.06 (4)	−1.86 (1)	−0.70 (4)

[a] The form of the anisotropic 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] Standard deviations of the least significant figures are given in parentheses here and in subsequent tables. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid group centers. The angles δ, ϵ, and η (in radians) have been defined previously.[15-17] [d] O4 represents the tetrahedral group of the perchlorate oxygen atoms.

TABLE II

Atom	x	y	z	B, Å^2
a. Derived Parameters for Ring Carbon Atoms[a]				
R1C1	0.1607 (5)	0.2177 (6)	0.3056 (4)	2.8 (2)
R1C2	0.2096 (5)	0.1712 (4)	0.2633 (5)	4.4 (2)
R1C3	0.2554 (4)	0.2362 (7)	0.2277 (4)	5.3 (3)
R1C4	0.2524 (6)	0.3476 (6)	0.2344 (5)	6.0 (3)
R1C5	0.2035 (6)	0.3941 (4)	0.2767 (5)	6.3 (3)
R1C6	0.1577 (4)	0.3291 (6)	0.3123 (4)	4.4 (2)
R2C1	0.1734 (4)	0.0404 (5)	0.4165 (4)	3.3 (2)
R2C2	0.2553 (4)	0.0712 (4)	0.4496 (5)	4.0 (2)
R2C3	0.3098 (3)	0.0064 (6)	0.5076 (5)	4.6 (3)
R2C4	0.2824 (4)	−0.0891 (6)	0.5326 (4)	5.5 (3)
R2C5	0.2006 (5)	−0.1198 (5)	0.4996 (5)	5.5 (3)
R2C6	0.1461 (3)	−0.0551 (6)	0.4416 (5)	4.1 (2)
R3C1	0.0585 (6)	0.2094 (7)	0.4148 (4)	3.1 (2)
R3C2	0.0881 (5)	0.1976 (7)	0.4995 (4)	4.3 (2)
R3C3	0.0562 (5)	0.2605 (6)	0.5494 (3)	5.3 (3)
R3C4	−0.0053 (6)	0.3352 (7)	0.5148 (4)	5.3 (3)
R3C5	−0.0349 (5)	0.3471 (7)	0.4302 (5)	5.4 (3)
R3C6	−0.0030 (4)	0.2842 (5)	0.3802 (3)	4.2 (2)
b. Derived Parameters for Perchlorate Group Oxygen Atoms				
O2	0.501 (3)	0.034 (1)	0.192 (1)	11.3 (7)
O3	0.473 (4)	0.215 (2)	0.208 (1)	11.1 (7)
O4	0.581 (1)	0.129 (5)	0.306 (1)	18.5 (13)
O5	0.445 (1)	0.085 (4)	0.294 (1)	9.9 (6)

[a] C1 is attached to P; other C atoms are numbered in succession so that C4 is *para* to C1.

All these calculations had only marginal effects on the positional parameters of the cation. The nitrogen and oxygen parameters were most affected. We feel that, in view of the disorder of the perchlorate group, the standard deviations of the bond lengths and angles associated with the nitrogen and oxygen atoms may be optimistic, but not by more than a factor of 2. The thermal parameters of the perchlorate oxygen atoms in the final model reflect the disparity in the peak heights found in the difference Fourier map. Why one oxygen atom should be vibrating more than the other three is not obvious from the mode of packing of the ions.

The value of R_2 obtained from the final cycle of least-squares refinement shows no dependence on $|F_o|$ or on $\lambda^{-1} \sin \theta$; thus the choice of p of 0.04 is essentially correct. Comparison of the final values of $|F_o|$ and $|F_c|$ suggests that no correction for secondary extinction is necessary. The error of an observation of unit weight is 1.59 electrons.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement are given in Table I, along with the associated standard deviations as estimated from the inverse matrix. The positional parameters of the perchlorate group oxygen atoms and the ring carbon atoms which may be derived from the data in Table I are presented in Table IIa and b together with their thermal parameters as obtained from the last cycle of least-squares refinement. The final values of $5|F_o|$ and $5|F_c|$ (in electrons) are given in Table III; only the 1597 reflections which were used in the refinement are listed in this table. Of the 285 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$ 284 had $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$. The reflection 919 had $|F_o^2 - F_c^2| = 5.7\sigma(F_o^2)$.

Description of Structure

The crystal structure consists of discrete monomeric ions, with the cation on and the anion disordered about crystallographically imposed twofold axes of symmetry. The nearest contact between the iridium atom and the perchlorate oxygen fragments is 3.98 Å.

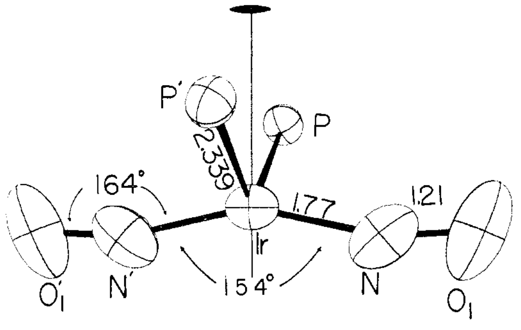

Figure 1.—The inner coordination sphere of the cation. Atoms related by the twofold axis are represented by X and X'.

The inner coordination geometry of the cation is shown in Figure 1 and a stereoscopic view of the cation is shown in Figure 2.

A selection of distances and angles is given in Table

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×5) IN ELECTRONS FOR $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$

K	L	FO	FC
***** H = 0 *****			
0	2	1937	1787
0	4	2451	2343
0	6	1086	1062
0	8	1079	1076
0	10	1001	988
0	12	928	900
0	14	440	404
0	16	519	484
2	0	1183	1113
2	1	1405	1339
2	2	978	960
2	3	517	504
2	4	929	925
2	5	520	487
2	6	860	869
2	7	273	260
2	8	778	813
2	9	703	723
2	10	844	847
2	11	474	487
2	12	629	596
2	13	354	335
2	14	481	473
2	16	370	370
4	0	587	559
4	1	893	874
4	2	600	598
4	3	632	631
4	4	491	486
4	5	665	661
4	6	696	729
4	7	586	548
4	8	367	398
4	9	551	553
4	11	424	434
4	12	234	230
4	13	377	372
4	14	388	395
4	15	386	376
6	0	577	614
6	1	947	897
6	2	476	472
6	3	915	939
6	4	307	332
6	5	1138	1166
6	7	719	785
6	8	404	425
6	9	244	238
6	11	348	335
6	12	365	384
6	13	462	430
6	14	151	123
8	0	301	328
8	1	651	671
8	2	224	247
8	3	676	709
8	5	482	492
8	6	180	194
8	7	751	765
8	8	181	181
8	9	606	646
8	11	484	478
10	0	195	203
10	1	779	803
10	2	173	198
10	3	511	531
10	5	371	359
10	6	240	277
10	7	380	409
10	9	388	371
12	0	447	421
12	1	300	280
12	2	302	311
12	3	309	300
***** H = 1 *****			
1	-16	345	321
1	-14	378	426
1	-12	900	893
1	-11	194	180
1	-10	745	731
1	-9	162	139
1	-8	1060	1034
1	-7	305	268
1	-6	850	832
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3	-4	1285	1291
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3	-2	864	918
3	0	1215	1268
3	1	467	444
3	2	418	470
3	3	522	483
3	4	754	781
3	5	472	452
3	6	848	837
3	7	285	282
3	8	828	835
3	10	488	457
3	11	286	305
3	12	356	381
5	-15	258	251
5	-14	283	263
5	-13	631	609
5	-12	562	557
5	-11	462	453
5	-10	501	465
5	-9	687	670
5	-8	376	409
5	-7	573	567
5	-6	338	354
5	-5	703	693
5	-4	511	528
5	-3	908	876
5	-2	791	846
5	-1	1151	1195
5	0	234	232
5	1	573	554
5	2	308	308
5	3	551	558
5	4	507	522
5	5	617	663
5	6	429	462
5	7	625	629
5	8	418	410
5	9	618	624
5	10	334	354
5	11	361	381
7	-13	474	469
7	-11	480	484
7	-9	496	480
7	-8	295	314
7	-7	570	587
7	-6	288	263
7	-5	508	494
7	-3	956	954
7	-1	846	825
7	1	679	652
7	2	259	263
7	3	623	613
7	4	281	278
7	5	552	546
7	6	179	194
7	7	656	638
7	8	148	123
7	9	485	476
9	-11	370	358
9	-9	498	486
9	-7	669	680
9	-5	666	625
9	-3	393	380
9	-1	470	494
9	1	547	536
9	3	706	674
9	5	569	526
9	6	184	171
9	7	376	373
11	-6	352	337
11	-5	328	290
11	-4	211	186
11	-3	319	314
11	-2	255	219
11	-1	323	349
11	0	220	231
11	1	330	324
11	2	256	263
***** H = 8 *****			
0	-16	380	377
0	-14	303	322
0	-12	240	237
0	-10	954	1010
0	-8	1346	1309
0	-4	872	855
0	-2	1181	1221
0	0	899	986
0	2	1189	1294
0	4	964	1049
0	6	797	798
0	8	592	638
0	10	843	832
0	12	490	534
2	-16	366	357
2	-14	487	471
2	-13	139	107
2	-12	645	674
2	-11	181	198
2	-10	827	839
2	-9	685	682
2	-8	462	467
2	-7	596	613
2	-6	777	779
2	-5	250	237
2	-4	567	570
2	-3	156	175
2	-2	874	840
2	-1	276	308
2	0	733	747
2	1	468	555
2	2	601	613
2	3	602	649
2	4	907	955
2	6	865	901
2	8	466	489
2	9	271	216
2	10	551	543
2	11	372	310
4	-15	376	360
4	-14	381	352
4	-13	368	404
4	-12	402	410
4	-11	358	352
4	-10	315	339
4	-9	630	622
4	-8	372	397
4	-7	549	522
4	-6	492	505
4	-5	711	708
4	-4	746	730
4	-3	713	665
4	-2	1106	1108
4	-1	756	765
4	0	288	332
4	1	748	745
4	2	269	275
4	3	489	511
4	4	384	400
4	5	501	502
4	6	581	590
4	7	561	547
4	8	563	540
4	9	326	334
4	10	267	278
4	11	340	329
6	-13	352	363
6	-11	395	382
6	-10	278	287
6	-9	370	378
6	-8	268	221
6	-7	341	359
6	-6	283	266
6	-5	539	569
6	-4	307	304
6	-3	1150	1207
6	-2	273	277
6	-1	584	586
6	0	203	223
6	1	417	441
6	2	314	280
6	3	376	437
6	4	214	247
6	5	556	586
6	6	236	231
6	7	517	521
6	8	183	222
6	9	504	514
8	-11	296	313
8	-10	192	150
8	-9	439	459
8	-8	274	238
8	-7	453	458
8	-5	387	378
8	-3	334	310
8	-1	588	620
8	1	538	551
8	2	368	378
8	3	577	608
8	5	502	501
8	7	414	417
10	-8	178	156
10	-7	589	567
10	-5	448	456
10	-4	173	173
10	-3	504	492
10	-1	469	472
10	0	237	274
10	1	483	480
10	2	210	171
10	3	566	586
***** H = 9 *****			
1	-16	321	308
1	-13	360	317
1	-12	478	528
1	-11	151	64
1	-10	835	812
1	-9	231	277
1	-8	875	919
1	-7	158	151
1	-6	737	763
1	-5	179	176
1	-4	461	502
1	-2	1065	1035
1	0	757	751
1	1	357	312
1	2	853	832
1	3	208	185
1	4	782	760
1	6	388	421
1	8	638	627
1	10	495	501
1	11	164	207
3	-16	311	322
3	-14	436	449
3	-12	381	405
3	-11	283	270
3	-10	484	474
3	-9	405	374
3	-8	584	591
3	-7	305	331
3	-6	724	740
3	-5	223	236
3	-4	903	935
3	-3	366	384
3	-2	759	773
3	-1	606	613
3	0	510	530
3	1	505	489
3	2	393	405
3	3	624	638
3	4	672	637
3	5	139	136
3	6	731	723
3	7	233	252
3	8	723	699
3	10	260	286
5	-15	465	469
5	-14	303	318
5	-13	393	393
5	-12	196	240
5	-11	372	379
5	-10	409	431
5	-9	397	395
5	-8	318	338
5	-7	482	484
5	-6	365	357
5	-5	737	745
5	-4	794	752
5	-3	703	718
5	-2	513	473
5	-1	567	557
5	0	292	256
5	1	423	449
5	2	332	304
5	3	498	490
5	4	524	535
5	5	640	637
5	6	550	550
5	7	494	505
5	8	418	438
5	9	449	423
7	-13	398	340
7	-11	457	461
7	-10	215	208
7	-9	513	501
7	-8	256	279
7	-7	625	638
7	-5	673	694
7	-3	899	934
7	-1	481	475
7	0	378	417
7	1	590	600
7	2	239	228
7	3	541	532
7	5	625	600
7	6	141	86
7	7	552	532
9	-9	546	544
9	-7	365	323
9	-5	434	405
9	-3	359	328
9	-2	300	281
9	-1	511	507
9	0	172	141
9	1	668	623
9	2	167	166
9	3	476	478
9	4	169	139
***** H = 10 *****			
0	-16	388	359
0	-14	286	287
0	-12	774	770
0	-10	1031	1017
0	-8	1395	1380
0	-6	435	440
0	-4	916	921
0	-2	723	808
0	0	1034	1122
0	2	844	885
0	4	624	630
0	6	390	382
0	8	1036	1022
0	10	515	464
2	-16	273	270
2	-14	262	274
2	-13	251	227
2	-12	372	408
2	-11	563	542
2	-10	474	476
2	-9	590	554
2	-8	567	584
2	-7	252	228
2	-6	741	740
2	-5	289	274
2	-4	907	870
2	-3	299	333
2	-2	959	926
2	-1	649	660
2	0	880	854
2	1	586	610
2	2	713	728
2	3	350	353
2	4	643	623
2	6	621	633
2	7	240	187
2	8	555	510
2	9	353	359
2	10	413	395
4	-15	275	272
4	-14	223	258
4	-13	220	237
4	-12	220	219
4	-11	277	271
4	-10	151	139
4	-9	349	373
4	-8	397	409
4	-7	412	419
4	-6	577	579
4	-5	535	518
4	-4	472	493
4	-3	368	347
4	-2	349	384
4	-1	469	440
4	0	125	126
4	1	503	504
4	2	309	330
4	3	396	407
4	4	448	432
4	5	344	358
4	6	500	515
4	7	463	467
4	8	381	375
4	9	222	249
6	-13	274	267
6	-11	288	307
6	-10	212	268
6	-9	338	323
6	-8	303	283
6	-7	450	450
6	-5	759	730
6	-4	372	370
6	-3	661	704
6	-2	166	104
6	-1	192	210
6	0	353	376
6	1	386	394
6	2	152	149
6	3	522	548
6	4	207	226
6	5	567	557
6	6	202	214
6	7	463	464
8	-11	282	307
8	-9	400	392
8	-7	433	447
8	-5	594	581
8	-3	502	503
8	-1	737	746
8	0	250	235
8	1	696	698
8	3	430	441
8	5	404	410
10	-5	225	227
10	-3	333	314
10	-1	410	370
***** H = 11 *****			
1	-15	174	145
1	-14	238	280
1	-13	185	144
1	-12	421	430
1	-11	341	316
1	-10	549	573
1	-9	274	264
1	-8	518	535
1	-6	402	423
1	-5	112	94
1	-4	682	672
1	-3	189	140
1	-2	682	666
1	0	859	827
1	1	388	405
1	2	605	615
1	4	265	285
1	6	604	593
1	8	525	535
1	9	178	129
3	-14	392	389
3	-13	236	208
3	-12	230	203
3	-11	292	311
3	-10	408	426
3	-9	201	231
3	-8	692	727
3	-7	213	221
3	-6	884	916
3	-5	261	290
3	-4	616	604
3	-3	363	413
3	-2	516	526
3	-1	425	464
3	0	471	482
3	1	380	377
3	2	683	666
3	4	549	539
3	5	270	236
3	6	655	621
3	7	206	200
3	8	388	386
5	-13	317	262
5	-12	233	233
5	-11	207	201
5	-10	292	321
5	-9	395	392
5	-8	397	384
5	-7	534	527
5	-6	582	575
5	-5	805	821
5	-4	498	476
5	-3	368	336
5	-2	331	359
5	-1	460	457
5	0	252	228
5	1	555	579
5	2	413	410
5	3	524	518
5	4	400	414
5	5	599	602
5	6	338	314
5	7	379	388
7	-11	363	374
7	-10	145	114
7	-9	365	356
7	-7	570	570
7	-5	557	600
7	-3	480	423
7	-2	364	366
7	-1	470	454
7	0	221	179
7	1	511	477
7	3	578	585
7	5	511	477
9	-8	138	118
9	-7	313	326
9	-6	205	207
9	-5	409	360
9	-3	441	456
9	-1	546	565
9	1	428	432
***** H = 12 *****			
0	-14	467	511
0	-12	603	604
0	-10	545	553
0	-8	490	484
0	-6	529	553
0	-4	750	757
0	-2	909	929
0	0	966	981
0	2	668	610
0	4	425	415
0	6	607	551
0	8	661	650
2	-14	414	378
2	-13	292	288
2	-12	337	328
2	-11	393	385
2	-10	510	525
2	-8	606	586
2	-6	805	793
2	-5	272	283
2	-4	613	584
2	-3	414	419
2	-2	643	610
2	-1	512	512
2	0	550	535
2	1	202	192
2	2	469	458
2	4	368	404
2	5	235	207
2	6	541	558
2	7	228	241
4	-13	283	270
4	-11	286	335
4	-10	184	174
4	-9	292	290
4	-8	461	493
4	-7	632	619
4	-6	618	613
4	-5	366	391
4	-4	292	312
4	-3	429	418
4	-2	199	218
4	-1	569	545
4	0	438	457
4	1	478	497
4	2	482	510
4	3	409	395
4	4	460	470
4	5	448	454
4	6	213	268
6	-11	252	233
6	-10	150	122
6	-9	340	332
6	-8	194	169
6	-7	482	495
6	-5	551	543
6	-4	270	246
6	-3	270	292
6	-1	361	372
6	1	446	469
6	3	630	605
6	4	181	160
6	5	432	431
8	-9	313	307
8	-7	442	425
8	-5	372	386
8	-3	314	310
8	-2	260	313
8	-1	473	466
8	1	331	314
***** H = 13 *****			
1	-14	353	342
1	-12	405	421
1	-11	181	110
1	-10	316	332
1	-9	216	197
1	-8	358	357
1	-7	229	206
1	-6	618	627
1	-4	633	645
1	-3	202	188
1	-2	661	696
1	0	509	538
1	2	319	345
1	4	484	452
1	6	433	460
3	-14	297	275
3	-13	326	309
3	-12	246	226
3	-11	273	280
3	-10	332	338
3	-8	711	739
3	-7	275	276
3	-6	500	524
3	-5	194	184
3	-4	404	401
-6	1	620	626
3	-3	360	362
3	-2	380	385
3	-1	382	369
3	0	669	609
3	2	548	507
3	3	276	272
3	4	573	513
3	5	247	271
3	6	244	243
5	-11	293	284
5	-10	169	180
5	-9	466	440
5	-8	364	399
5	-7	600	596
5	-6	285	261
5	-5	404	365
5	-4	460	416
5	-3	266	287
5	-2	150	138
5	-1	471	450
5	0	441	387
5	1	471	474
5	2	372	346
5	3	524	502
5	4	325	291
7	-9	352	381
7	-7	514	522
7	-5	379	373
7	-4	169	153
7	-3	454	427
7	-1	488	471
7	1	471	469
***** H = 14 *****			
0	-14	485	461
0	-12	326	322
0	-10	223	234
0	-8	424	420
0	-6	717	739
0	-4	913	921
0	-2	681	695
0	0	518	516
0	2	411	379
0	4	471	458
2	-13	396	363
2	-12	322	312
2	-10	319	358
2	-9	196	177
2	-8	436	444
2	-6	435	401
2	-5	557	531
2	-4	501	502
2	-3	419	405
2	-2	543	560
2	-1	281	259
2	0	453	441
2	2	498	531
2	3	267	237
2	4	491	492
4	-12	211	167
4	-11	170	160
4	-10	350	355
4	-9	327	330
4	-8	354	363
4	-7	379	362
4	-6	355	374
4	-5	165	143
4	-3	458	447
4	-2	279	275
4	-1	280	279
4	0	384	402
4	1	330	323
4	2	430	393
4	3	363	334
6	-9	431	428
6	-8	144	134
6	-7	299	332
6	-5	244	251
6	-4	292	259
6	-3	347	339
6	-2	249	219
6	-1	355	363
6	1	448	433
***** H = 15 *****			
1	-12	249	258
1	-10	245	253
1	-8	263	284
1	-7	247	217
1	-6	502	515
1	-5	323	302
1	-4	594	600
1	-3	197	175
1	-2	393	382
1	0	268	316
1	2	417	397
3	-10	412	395
3	-8	404	381
3	-6	292	293
3	-5	236	262
3	-4	311	330
3	-3	302	347
3	-2	514	484
3	0	484	459
3	2	457	409
5	-9	395	441
5	-7	169	188
5	-6	290	323
5	-5	256	242
5	-4	242	220
5	-3	300	324
5	-2	370	363
5	-1	347	338
5	0	270	282
***** H = 16 *****			
0	-10	330	316
0	-8	454	462
0	-6	739	743
0	-4	482	514
0	-2	321	302
0	0	409	376
2	-10	240	245
2	-8	274	277
2	-7	228	216
2	-6	289	296
2	-5	367	343
2	-4	509	503
2	-2	470	460
2	-1	131	98
2	0	405	401
4	-7	261	245
4	-5	219	247
4	-4	259	217
4	-3	300	331
4	-2	335	302
***** H = 17 *****			
1	-7	172	153
1	-6	447	447
1	-4	308	291
1	-3	188	151

IV. The root-mean-square amplitudes of vibration of those atoms refined anisotropically are listed in Table V. The directions of vibration of all but the chlorine atom are shown in Figure 1. The bond distances given in Table IV can be corrected for thermal motion using the "riding" and "independent" models of Busing and Levy,[18] but the differences between various bond lengths remain essentially the same when either of these corrections is applied.

The Ir–P distance, 2.339 (3) Å, is very similar to that found for the isoelectronic tetrahedral complex $Pt(CO)(P(C_6H_5)_3)_3$,[19] 2.35 (1) Å, and for IrCl(CO)-

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

(19) (a) V. G. Albano, P. L. Bellon, and V. Scatturin, Inorganica Chimica Acta, 1st International Symposium, New Aspects of the Chemistry of Metal Carbonyls and their Derivatives, Venice, Italy, Sept 1968; (b) V. G. Albano, G. M. B. Ricci, and P. L. Bellon, *Inorg. Chem.*, **8**, 2109 (1969).

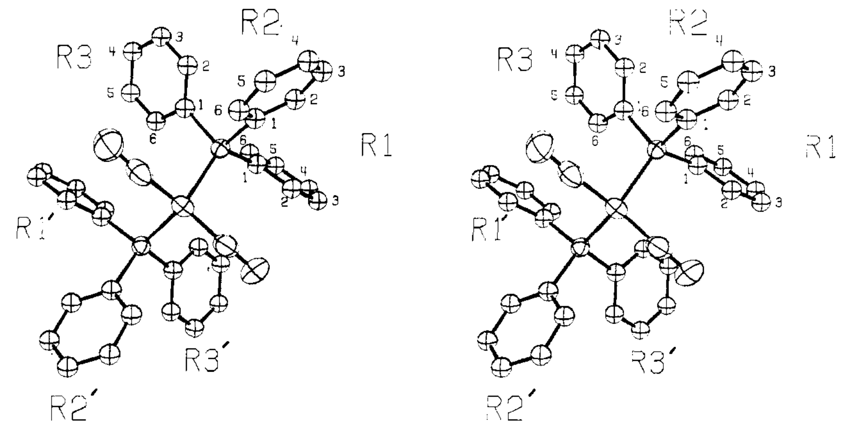

Figure 2.—A stereoscopic view of the cation $Ir(NO)_2(P(C_6H_5)_3)_2^+$. The isotropic thermal parameters of the carbon atoms have all been set to 3.0 Å². For other atoms 50% probability ellipsoids are shown.

Table IV

Selected Distances and Angles[a]

Cation intramolecular dist, Å		Angle, deg	
Ir–P	2.339 (3)	P–Ir–P′	116.3 (2)
Ir–N	1.771 (12)	P–Ir–N	100.4 (3)
Ir–O1	2.954 (11)	P–Ir–N′	93.2 (3)
P–N	3.178 (11)	Ir–N–O1	163.5 (10)
P–N′	3.011 (10)	N–Ir–N′	154.2 (7)
N–N′	3.452 (25)	P–Ir–O1	97.5 (2)
N–O1	1.213 (13)	P–Ir–O1′	89.2 (2)
P–C (av of 3)	1.814 (7)	O1–Ir–O1′	167.5 (5)
P–P′	3.973 (6)	Ir–P–R1C1	114.2 (3)
Ir–H(R2H6)	3.08	Ir–P–R2C1	110.4 (2)
N–H(R1H2)	2.80	Ir–P–R3C1	114.0 (3)
N–H(R2H6)′	2.61	R1C1–P–R2C1	104.7 (3)
O1–H(R1H2)	2.67	R1C1–P–R3C1	108.1 (4)
O1–H(R2H6)′	3.02	R2C1–P–R3C1	104.6 (3)
Intermolecular dist, Å			
N–H(R1H4)	3.04	Dihedral angle between P–Ir–P′ and N–Ir–N′	85.7 (3)
O1–H(R3H2)	2.79		

[a] X and X′ represent atoms related by the twofold axis of symmetry.

Table V

Root-Mean-Square Amplitudes of Vibration (Å)[a]

Atom	Min	Intermed	Max
Ir	0.1879 (10)	0.1966 (11)	0.2315 (10)
P	0.186 (4)	0.194 (4)	0.204 (4)
Cl	0.217 (7)	0.287 (6)	0.351 (7)
N	0.208 (14)	0.232 (14)	0.325 (14)
O1	0.225 (14)	0.297 (12)	0.449 (14)

[a] Measured along the principal axes of the thermal ellipsoids.

$(SO_2)(P(C_6H_5)_3)_2$,[16] 2.359 (9) and 2.328 (8) Å, but it is shorter than those found for $IrI(O_2)(CO)(P(C_6H_5)_3)_2$,[15] 2.391 (8) and 2.386 (8) Å, and $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$, 2.408 (3) and 2.407 (3) Å.[1] The Ir–N and N–O distances are 1.771 (12) and 1.213 (13) Å, respectively. The bond angles around iridium are: N–Ir–N′, 154.2 (7)°; P–Ir–P′, 116.3 (2)°; P–Ir–N′, 93.2 (3)°; P–Ir–N, 100.4 (3)°. The dihedral angle between the planes P–Ir–P′ and N–Ir–N′ is 85.7 (3)°.

As one of the aims of this work was to define the oxidation state of the metal by examining the stereochemistry of the complex, some results obtained by other workers for similar d^{10} and d^8 complexes will be described. The isoelectronic d^{10} complex $Pt(CO)(P(C_6H_5)_3)_3$ shows only small distortions from the ideal tetrahedral geometry (P–Pt–P = 104.7 (5)° and P–Pt–C = 113.7 (5)° in a trigonal space group; P–Pt–P = 111.4 (3)° and P–Pt–C = 107 (1)° in a monoclinic space group).[19] However, the complexes $Cu(NO_3)(P(C_6H_5)_3)_2$ (P–Cu–P = 131.1°),[20] $Cu(BH_4)(P(C_6H_5)_3)_2$ (P–Cu–P = 123.3°),[21] and the phosphine oxide and arsine oxide complexes $[CuCl(OP(C_6H_5)_2)_2C_2H_4)]_n$ (Cl–Cu–O = 140.2°)[22] and $HgCl_2(OAs(C_6H_5)_3)_2$ (Cl–Hg–Cl = 146.6°, O–Hg–O = 92.5°)[23] show large distortions from the ideal. In fact many four-coordinate complexes of mercury(II) show large distortions from the ideal tetrahedral geometry.[24]

In general *trans* square-planar d^8 complexes of the platinum metals show smaller distortions from the ideal. For example the following bond angles have been reported for *trans*-$RhClCS(P(C_6H_5)_3)_2$;[25] P–Rh–Cl, 89.4 (1) and 87.3 (1)°; P–Rh–C, 91.6 (2) and 92.0 (2)°; Cl–Rh–C, 174.5 (6)°; P–Rh–P, 175.6 (1)° Similar bond angles have been reported for *trans*-$[PtCl(CO)(P(C_2H_5)_3)_2][BF_4]$.[26]

The bond angles observed for $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ (see Table IV) are intermediate between those expected for ideal tetrahedral and square-planar geometries. From a consideration of bond angles it is impossible to decide unambiguously on the oxidation state of the metal because d^{10} tetrahedral complexes often show large distortions from the ideal (see above), and although the square-planar d^8 complexes which have been studied show only small distortions, the effect of two electrons in antibonding nitrosyl orbitals is difficult to evaluate.

However, the following factors lead us to favor the d^{10} formulation. The iridium–nitrogen bond length (1.771 (12) Å) is 0.2 Å shorter than that found for $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$,[1,2] where the nitrosyl

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ligand is behaving as a Lewis acid, but is in the range found for NO^+ complexes (1.57–1.78 Å; see Table VI of ref 2). The Ir–N–O bond angle (163.5 (10)°), though far from 180°, is just within the range observed for NO^+ complexes (see Table VI of ref 2). Finally the large N–Ir–N′ bond angle can perhaps be accounted for by nonbonded interactions. The nonbonded contacts between the nitrosyl group and the *ortho*-hydrogen atoms of the triphenylphosphine groups are near those predicted from van der Waals radii.[27] We have calculated that these contacts would decrease considerably if the N–Ir–N′ bond angle were 109° 28′. The importance of these steric factors might be evaluated if the crystal structure of $Pt(CO)_2(P(C_6H_5)_3)_2$ were determined.

We have made many attempts to isolate crystals of the five-coordinate complex $IrI(NO)_2(P(C_6H_5)_3)_2$. However each time mixtures of $IrI(NO)_2(P(C_6H_5)_3)_2$ and $IrI_2(NO)(P(C_6H_5)_3)_2$ have been obtained. We wish to speculate that $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ is able to react with lithium halides to give these unusual five-coordinate complexes for two reasons. First, the geometry of the cation is intermediate between tetrahedral and square planar and therefore the activation energy for formation of a five-coordinate complex is smaller than that for a relatively undistorted tetrahedral complex such as $Pt(CO)(P(C_6H_5)_3)_3$. Second, nitrosyl is an amphoteric ligand and the two electrons which exceed the inert-gas rule can be accommodated in antibonding nitrosyl orbitals rather than in metal–ligand σ-antibonding orbitals. The fact that nitrosyl is able to behave like an electron well in such reactions suggests some very interesting catalytic possibilities.

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The Crystal and Molecular Structure of Hexakis(urea)titanium(III) Iodide

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The crystal structure of hexakis(urea)titanium(III) iodide, $Ti[OC(NH_2)_2]_6I_3$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined to a final unweighted R factor of 0.067 and a weighted R factor of 0.064 for 499 independent nonzero reflections. The salt crystallizes in the rhombohedral space group $R\bar{3}c$ with six formula units in a hexagonal unit cell of dimensions $a = 17.67$ (2) Å and $c = 14.15$ (2) Å. The structure consists of octahedral complex ions having rigorous D_3 point symmetry and essentially linear arrays of iodide ions parallel to the crystallographic threefold axis. The titanium–oxygen bond distance is 2.014 (5) Å. There are significant distortions of the coordination polyhedron from the idealized O_h symmetry and from the D_{3d} model often assumed for trigonally distorted octahedral complexes. The three independent O–Ti–O angles are 90.5 (2), 86.4 (3), and 92.8 (3)°, and the angles between successive pairs of Ti–O bonds viewed in projection along the threefold axis are 54.4 and 65.6°. The stability of this complex to aerial oxidation apparently arises from intramolecular hydrogen bonding involving the urea molecules and also hydrogen bonds involving the iodide ions. The d-orbital energy level sequence for a crystal (ligand) field of D_3 symmetry, where the inclination of metal–ligand bond to the threefold axis is 54.74°, can be described entirely in terms of the parameter Dq, and the ground state for a d^1 complex ion is $^2A_1$.

Introduction

Coordination compounds of titanium(III) have long occupied a prominent place in the development at various levels of sophistication of crystal and ligand field theory. Despite this fact, however, there is a paucity of accurate structural information from X-ray measurements on their detailed stereochemistry in the solid, principally because the majority of such compounds are highly unstable with respect to oxidation and many hydrolyze rapidly in the presence of moisture. The isolation and handling of suitable single crystals is thus a difficult operation.

One of the more stable species is the hexakis-urea complex ion which was first isolated as the perchlorate salt[2] and subsequently as the iodide.[3] One of the interesting features of the latter compound is its marked stability relative to other titanium(III) species, and a preliminary report of the crystal structure, in the form of a two-dimensional projection, has already been given.[4] This preliminary work did not reveal the origin of the stability of the complex, however, and we have therefore carried out a more detailed study, both to investigate this point and to assess the nature of the distortion from regular octahedral symmetry, which is indicated by the observed variation

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