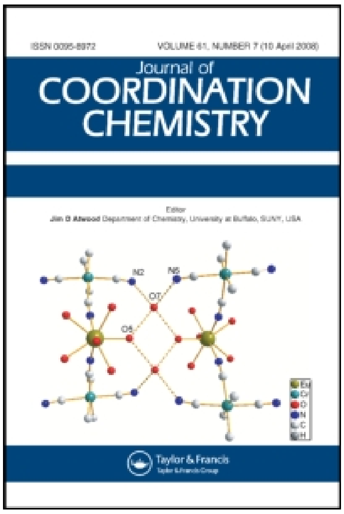

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THE CRYSTAL AND MOLECULAR STRUCTURE OF CHLORODICARBONYLPYRIDYLIRIDIUM(I) $IrCl(CO)_2(C_5H_5N)$

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INTRODUCTION

In a continuing investigation of the structural properties of the heavy d^8 metal complexes[1] in which metal-metal interactions are indicated, the crystal structure of chlorodicarbonylpyridyliridium(I) has been determined. In the past the square-planar complexes of Ir(I) and Rh(I) have most commonly been proposed to form linear chains,[2] the validity of which has been shown in several studies,[3,4] However, the dimeric nature of the complex 3-methyl-2,4-pentanedionatodicarbonyliridium(I)[1] has subsequently cast doubt on the generality that chain interactions can always account for the properties of this type of complex. This question has thus prompted our investigation of other square-planar d^8 complexes such as that decribed in this paper. This complex, $IrCl(CO)_2$ (pyridine), was first prepared and characterized by Hieber and Frey.[5] Like dicarbonylacetylacetonatoiridium(I)[4], electrical conductivity studies of this complex[6] are also highly indicative of metal-metal interactions. It is thus important to reveal the actual structural details. The results of our studies are given here.

EXPERIMENTAL

Collection and Reduction of the X-ray Data

Crystals of $IrCl(CO)_2(C_5H_5N)$ were supplied by Dr. J. P. Collman in coordination with studies in progress in that laboratory. Precession photographs of the $0kl, hk0, lkl, hkl, 2kl$, and $hk2$ zones established the crystals as belonging to monoclinic symmetry. The observed systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h = 2n + 1$) are consistent with the space group $C_{2h}{}^5 - P^2{}_1/a$. The monoclinic lattice parameters were obtained from the precession photographs and refined by a least-squares refinement[7] of the setting angles, χ, ϕ, and 2θ, for twelve individually centered reflections using a Picker four-circle x-ray diffractometer. The unit cell constants (at 23°C., Mo $K_{\alpha 1}$) thus obtained are $a = 17.58(6)$, $b = 7.16(2)$, $c = 11.65(4)$, and $\beta = 142.9(1)°$. Due to solubility problems, the density could not be accurately determined by floation but was found, at least, to be in excess of $2.5\ g \cdot cm^{-3}$. Thus the density of $2.75\ g \cdot cm^{-3}$ calculated on the basis of four molecules per unit cell appears to be quite reasonable, the validity of which is supported further by the actual structural results.

Diffraction data were collected with a near rectangular crystal of dimensions 0.38 x 0.13 x 0.03 mm mounted on a glass fiber normal to the [010] planes and parallel to the longest dimension. The face with the shortest dimension belongs to the [001] planes, while those of length 0.13 mm are $[\bar{2}01]$ and $[20\bar{1}]$. The data were collected on a Picker automatic diffractometer by use of procedures described elsewhere.[8,9] A take-off angle of 1.8° was employed. The diffracted beam was filtered through 3.0 mm Nb foil. The counter aperture was 5 x 5 mm square and was positioned 38 cm from the crystal. The pulse-height analyzer was set to admit approximately 95% of the Mo K_α peak. Intensity data were collected using the $\theta - 2\theta$ scan method using a scan range of 0.75 to $-0.88°$ about the peak for reflections with $2\theta \leqslant 35°$ with allowances made for the $K_{\alpha_1} - K_{\alpha_2}$ split at values higher than 35°. The scan rate was 1/1° per minute, and stationary background counts of 20 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded 10,000 counts/sec, however, only four reflections required attenuators. Three reflections chosen to lie in different regions of reciprocal space, were monitored at regular intervals during the data collection. No reduction in intensity of these monitors was observed during the course of

TABLE I
Atomic positional and thermal parameters[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2
Ir	0.22636(4)	0.1250(2)	-0.03698(5)	0.00603(5)	0.02147(12)	0.01617(11)	0.00040(13)	0.00816(6)	0.0013(2)	
Cl	0.3050 (2)	0.1307(8)	0.2462 (4)	0.0093 (3)	0.0283 (8)	0.0212 (6)	0.0014 (6)	0.0123 (4)	0.0010(8)	
C(1)	0.1597 (9)	0.116 (3)	-0.260 (2)	0.0058 (10)	0.027 (3)	0.017 (3)	0.000 (2)	0.0071 (14)	0.003 (3)	
O(1)	0.1204 (8)	0.105 (2)	-0.4010 (11)	0.0103 (9)	0.037 (3)	0.018 (2)	0.001 (2)	0.0103 (12)	0.002 (2)	
C(2)	0.0668 (11)	0.113 (3)	-0.169 (2)	0.0083 (13)	0.028 (4)	0.019 (2)	-0.003 (3)	0.011 (2)	0.000 (4)	
O(2)	-0.0326 (8)	0.114 (2)	-0.2548 (12)	0.0073 (8)	0.038 (3)	0.026 (2)	0.000 (2)	0.0108 (12)	0.005 (2)	
N	0.4132 (8)	0.134 (2)	0.1198 (11)	0.0076 (8)	0.019 (2)	0.017 (2)	0.000 (1)	0.0100 (13)	0.000 (2)	
C(3)	0.0120 (11)	0.433 (1)	0.297 (1)	0.0078 (12)	0.014 (3)	0.014 (3)	-0.0017 (12)	0.008 (2)	-0.001 (2)	
C(4)	0.0133 (1)	0.431 (2)	0.398 (2)	0.0072 (11)	0.022 (4)	0.022 (3)	-0.0029 (14)	0.010 (2)	-0.004 (2)	
C(5)	0.1500 (9)	0.356 (2)	0.314 (2)	0.0062 (11)	0.022 (3)	0.024 (3)	0.001 (2)	0.009 (2)	0.003 (2)	
C(6)	0.0503 (12)	0.288 (2)	0.132 (2)	0.0096 (14)	0.035 (4)	0.025 (3)	0.001 (2)	0.013 (2)	0.000 (3)	
C(7)	0.4352 (12)	0.207 (2)	0.042 (2)	0.0103 (14)	0.031 (4)	0.022 (3)	-0.003 (2)	0.012 (2)	0.002 (2)	
H(1)[c]	-0.0053	0.4855	0.3571							4.5
H(2)	0.2057	0.4842	0.5316							5.2
H(3)	0.2381	0.3551	0.3858							5.2
H(4)	0.0676	0.2346	0.0735							6.2
H(5)	-0.1473	0.2391	-0.0931							5.9

[a] Numbers in parentheses in all tables as well as the text are estimated standard deviations in the least significant figures.

[b] The form of the anisotropic thermal ellipsoid is exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

[c] Coordinates of the hydrogen atoms are calculated values as discussed in the text. Thermal parameters were set as one unit greater than that of the carbon to which it is attached if isotropic. The number of the ring carbon and attached hydrogen correspond.

the collection, and the greatest average deviation was only 1.3%.

A total of 1325 reflections were collected with $2\theta \leqslant 45°$. The data were corrected for background, Lorentz-polarization, and absorption (the absorption coefficient, $\mu = 163.3\ \text{cm}^{-1}$ and the transmission factors range from 1.67 to 6.76) by the usual methods.[8,9] The p factor in the expression

$$\sigma(\mathrm{I}) = [\mathrm{C} + 0.25(t_c/t_b)^2(\mathrm{B}_1 + \mathrm{B}_2) + (p\mathrm{I})^2]^{1/2}$$

was assigned the value of 0.05. From counting statistics, 838 of the 1325 independent reflections were above background by more than three standard deviations and thus judged observed.

Solution and Refinement of the Structure

The structure was solved by direct application of Patterson, Fourier, and least-squares methods. All least-squares refinements were carried out on F. minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The weights, w, were intially taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factor for Ir was taken from Cromer and Waber,[10] that for H from Stewart, Davidson, and Simpson,[11] and all others from the appropriate tabulation.[12] The structure factor calculations for F_c include allowance for anomalous scattering for both Ir and Cl, the values of which were taken from the tabulation of Cromer.[13] Only the 838 independent intensities were used in the refinement of the structure.

Initially, the Ir and Cl atoms were assigned isotropic thermal parameters. Least-squares refinement of the positional and thermal parameters and a scale factor yielded the agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.276$ and $R_2 = [\Sigma w(|F_o| - |F_c|^2/\Sigma w|F_o|^2]^{1/2} = 0.328$. Positional parameters for the ten carbon, nitrogen, and oxygen atoms were obtained, and all twelve non-hydrogen atoms were then refined with anisotropic thermal parameters. In the final stages of refinement, the five hydrogen atom positions were calculated based upon a trigonal arrangement (C – H = 1.08 Å). A virtual weighting scheme, $\sigma_F{}^o = A + B|F_o| + C|F_o|^2$, was also used with $A = 1.47$, $B = -0.012$ and $C = 0.0002$. The last cycle of least-squares refinement converged to $R_1 = 0.025$ and $R_2 = 0.029$ with the largest parameter shift equal to 0.21σ. A final difference Fourier map showed no peak higher than $1.1\ \text{e}\ \text{Å}^{-3}$ with a $\sigma(\Delta\rho)$ of $0.13\ \text{e}\ \text{Å}^{-3}$.

The atomic positional and thermal parameters derived from the last cycle of least-squares refinement are listed in Table I along with the associated standard deviations. Intramolecular distances and angles are tabulated in Tables II and III, respectively.

TABLE II
Intramolecular bond distances (Å)

Ir–Cl	2.342 (3)
Ir–C(1)	1.801 (14)
Ir–C(2)	1.825 (12)
Ir–N	2.133 (8)
C(1)–O(1)	1.170 (16)
C(2)–O(2)	1.129 (14)
N–C(3)	1.340 (13)
C(3)–C(4)	1.389 (17)
C(4)–C(5)	1.335 (17)
C(5)–C(6)	1.364 (17)
C(6)–C(7)	1.344 (19)
C(7)–N	1.333 (15)

TABLE III
Intramolecular bond angles (DEG)

C(1)–Ir–C(2)	89.1 (5)
C(1)–Ir–N	91.2 (4)
N–Ir–Cl	91.1 (3)
Cl–Ir–C(2)	88.6 (4)
Ir–C(1)–O(1)	176.6 (16)
Ir–C(2)–O(2)	176.6 (18)
Ir–N–C(3)	121.4 (8)
N–C(3)–C(4)	121.5 (11)
C(3)–C(4)–C(5)	118.3 (11)
C(4)–C(5)–C(6)	121.0 (11)
C(5)–C(6)–C(7)	118.2 (12)
C(6)–C(7)–N	123.3 (12)
C(7)–N–C(3)	117.8 (11)
C(7)–N–Ir	120.8 (8)

DESCRIPTION OF THE STRUCTURE

A view of the molecular configuration of chlorobiscarbonylpyridyliridium(I) is shown in Figure 1.

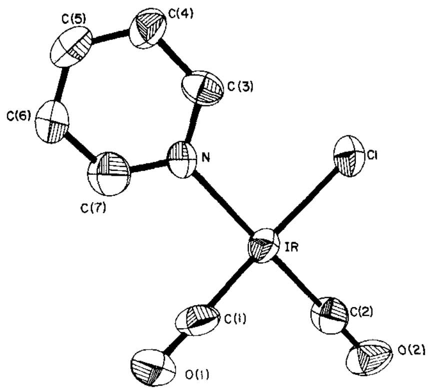

FIGURE 1 Numbering scheme and structure of chlorodicarbonylpyridyliridium(I).

TABLE IV
Molecular planes[a]

1. Plane containing Cl, N, C(1), and C(2)

Unit vector: $-0\ 0208x - 0.9990y - 0.0396z = -2.9422$

Atoms	*Distance to plane,* Å
Ir	0.012
O(1)	−0.061
O(2)	0.053
C(3)	−0.539
C(4)	−0.572
C(5)	−0.043
C(6)	0.492
C(7)	0.515

2. Plane containing N, C(3), C(4), C(5), C(6) and C(7)

Unit vector: $0.2324x + 0.9001y - 0.3684z = 5.4998$

Atoms	*Distance to plane,* Å
Ir	0.043
Cl	−1.014
O(1)	1.463
O(2)	0.083
C(1)	0.875
C(2)	0.100

3. Angles between planes

Planes	*Angles, deg*
1-2	27.2

[a] Unit weights were employed in the calculation. Equations of the planes are expressed with respect to coordinates (x, y, z) referred to an orthogonal system (A, B, C) oriented with A along a, B along b, and C in the direction of AxB.

The iridium coordination sphere is occupied by two *cis*-carbonyl groups, a chlorine atom, and the nitrogen atom of the pyridine ring. As is detailed in Table IV, the iridium atom is directly in the plane of the four ligands, resulting in a square-planar environment for the metal. The Ir-Cl distance [2.342(3) Å] and the Ir-C distances [av. 1.813(14)Å], found in Table II, agree reasonably well with the corresponding values determined in chloro-*cis*-dicarbonyl-(3, 5, 7-triphenyl-4H-1, 2-diazepine)rhodium(I)[14] of 2.335(2) Å and 1.855(15) Å respectively. The shorter M-C distance in $IrCl(CO)_2(C_5H_5N)$ is undoubtly a reflection of the changed electron distribution due to the different fourth ligand. Finally, the Ir-N bond distance of 2.133(8) Å appears to be quite reasonable.

An examination of the carbonyl groups reveal a normal arrangement, the oxygens deviating from linearity by only 3.4°. In addition, it is found that these oxygens and the carbon opposite the nitrogen atom in the pyridine ring are coplanar with the square of the metal. However, the pyridine ring, although planar in itself, is tilted from the square plane by 27.2° about a spindle imagined along the nitrogen atom and the carbon atom opposite it in the ring.

The most interesting aspect of this structure lies in the relationship of a molecular unit to its neighboring molecules. As is shown in Figure 2, this complex does indeed form almost linear chains of iridium atoms. The metal atoms along the chain are 3.602(12) Å apart with the Ir-Ir-Ir angle being 162.8(1)°. Also, represented in Figure 2 is the alternating arrangement of the pyridine rings. Considering single chains, a pyridine ring is never directly above the adjacent to another. Adjacent chains, however, are found to intersperse their carbonyl groups and pyridine rings between the neighboring molecules. Examination of the overlapping area in the direction of the chain reveals pairs of identical ligands from two chain alternating. The result of this arrangement is that every pyridine ring is adjacent to one other pyridine ring and one pair of carbonyl groups with the reverse grouping about each pair of carbonyls. Finally, it should be noted that the distance between metals in adjacent chains is in excess of 7 Å.

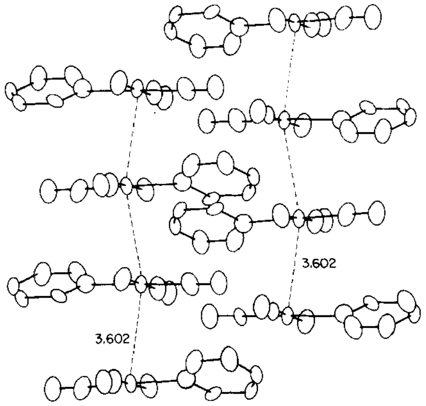

FIGURE 2 Crystal packing diagram showing the iridium chain structure.

DISCUSSION

Although only a minimal amount of information exists as to the extent and nature of the metal-metal interactions in rhodium and iridium d^8 complexes, one effect, which is observed in other metal complexes as well,[2] is most readily revealed in our studies. The formation of chain structures is exceedingly dependent upon the geometry of the individual molecular units. Being planar, both $Ir(CO)_2$ (acac)[4] and $Rh(CO)_2$(acac)[3] appear to form linear chains quite readily, as reflected in the short metal-metal distances of 3.20 and 3.27 Å respectively. In $Ir(CO)_2[(CH_3CO)_2CCH_3]$[1], which has a metal-metal distance of 3.29 Å, the additional methyl group appears to hinder approach from that side eliminating chain relations but not dimeric interactions on the non-hindered side of adjacent molecules. The complex, $IrCl(CO)_2(C_5H_5N)$, exhibits one other variation. While maintaining a near linear arrangement, the inter-layering of the tilted pyridine rings results in the much larger Ir-Ir separation of 3.60 Å. Thus interactions along the chain in this complex should be somewhat weaker than those found previously. It should be noted that metal-metal interactions between adjacent chains in all of these complexes appears quite unlikely. Thus it seems that the true structures of these complexes can be quite interesting and are very important in adequately understanding their known physical characteristics.

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