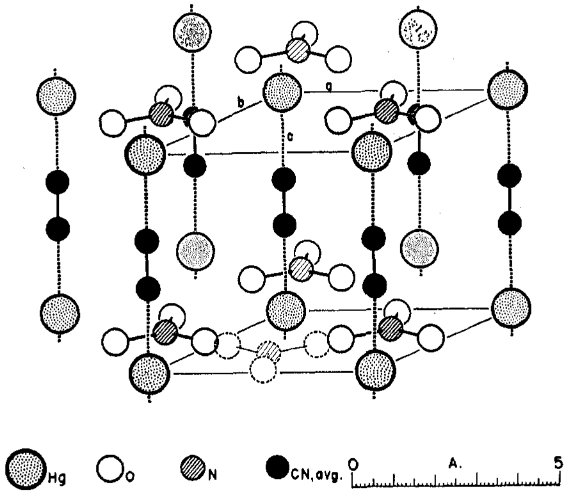

Figure 1.—The crystal structure of mercury(II) cyanonitrate.

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

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

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

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

Acknowledgment.—We wish to thank the National Science Foundation for its support of this research. Also, the diffractometer was purchased under the Chemistry Research Instruments Program of the National Science Foundation in cooperation with the Graduate Research Center of the University of Minnesota.

(18) D. Britton, *Perspect. Struct. Chem.*, **1**, 109 (1967).
(19) C. Mahon, *Inorg. Chem.*, **10**, 1813 (1971).
(20) S. D. Arora, W. N. Lipscomb, and M. C. Sneed, *J. Amer. Chem. Soc.*, **73**, 1015 (1951).
(21) W. N. Lipscomb, *Acta Crystallogr.*, **4**, 156 (1951).
(22) W. N. Lipscomb, *ibid.*, **4**, 266 (1951).
(23) L. Nijssen and W. N. Lipscomb, *ibid.*, **5**, 604 (1952).
(24) W. Rüdorff and L. Broderson, *Z. Anorg. Allg. Chem.*, **274**, 323 (1953).
(25) K. Aurivillius, *Ark. Kemi*, **24**, 151 (1965).

CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.,
MURRAY HILL, NEW JERSEY 07974

Mössbauer Effect Study of Molecular Adducts of *trans*-Bis(triphenylphosphine)iridium Carbonyl Chloride

BY H. H. WICKMAN* AND W. E. SILVERTHORN

Received December 15, 1970

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

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

---

* Address correspondence to this author at Department of Chemistry, Oregon State University, Corvallis, Oreg. 97331.

(1) L. Vaska, *Science*, **140**, 809 (1963).
(2) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).
(3) F. Wagner, G. Kaindl, P. Kienle, and H. J. Konnen, *Z. Phys.*, **207**, 500 (1967).
(4) A. Henberger, F. Pobell, and P. Kienle, *ibid.*, **205**, 503 (1967).
(5) U. Atzmony, E. R. Bauminger, D. Lebenbaum, A. Mustachi, S. Ofer, and J. H. Wernick, *Phys. Rev.*, **163**, 314 (1967).
(6) We thank R. B. Frankel of the National Magnet Laboratory, Cambridge, Mass., for assistance with the measurements.

TABLE I

ISOMER SHIFTS AND QUADRUPOLE INTERACTIONS IN VASKA-TYPE IRIDIUM COMPOUNDS[a]

	Type[c]	ΔE, cm/sec	δE,[b] cm/sec	Carbonyl freq,[b] cm^{-1}
		Square Planar Homologs		
(i) $IrCl(CO)((C_6H_5)_3P)_2$		0.774 ± 0.003	−0.049 ± 0.0015	1967
(ii) $IrBr(CO)((C_6H_5)_3P)_2$		0.692	−0.053	1972
		Molecular Adducts of (i)		
O_2	II	0.275	−0.083	2015
H_2	I	0.476	−0.019	2034 (D–D)
HCl	I	0.144	−0.030	2046
CH_3I	I	0.103	−0.054	2047
I_2	I	0.282	−0.093	2067
Cl_2	I	0.310	−0.102	2075

[a] The source was prepared by neutron irradiation of enriched osmium-192.[3] Data analysis employed a nonlinear least-squares fitting routine based on an algorithm of D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 11, 431 (1963) (SHARE distribution 3094), and adapted for Mössbauer data analysis by W. A. Burnette, C. S. Roberts, and D. N. E. Buchanan of Bell Laboratories. Owing to the source splitting each spectrum consisted of four lines, typical line widths being 0.048 cm/sec. [b] Isomer shifts are relative to iridium-193 in Os metal source. Source and absorber temperatures were 20.2°K. Subtract 0.054 mm/sec to obtain the shifts relative to iridium metal. [c] Reference 2.

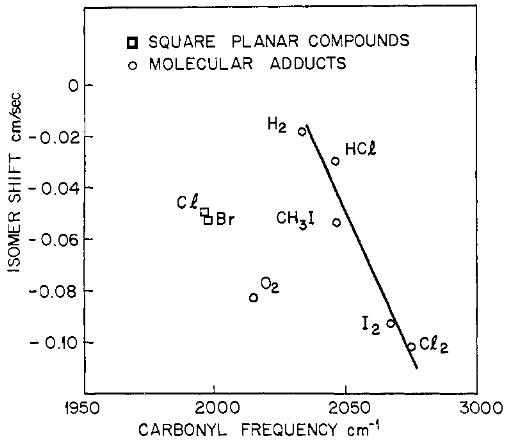

Figure 1.—Plot of isomer shifts *vs.* carbonyl frequencies in several iridium compounds.

hexagonal environment of iridium in osmium metal.

The Cl-VA–H_2, –HCl, –Cl_2, and –I_2 complexes were prepared by the method of Vaska and DiLazio.[7] The Cl-VA–O_2 complex was prepared by the method of ref 1. The Cl-VA–CH_3I complex was prepared by the method of Heck.[8] Cl-VA and Br-VA were purchased from Strem Chemicals, Inc., Danvers, Mass. All compounds were characterized by infrared spectroscopy. The Mössbauer patterns in all cases showed a clean quadrupole doublet (neglecting source splitting), indicative of a single molecular species.

The presence of covalent bonding in the iridium complexes implies that the changes resulting from molecular substitution ideally require for their interpretation knowledge of the molecular orbitals involving metal and ligand states. In a given bond, a relative increase of 6s character, or decrease of 5d character, can result in a larger value of $|\psi(0)|^2$, the net s-electron density at the nucleus. The former process is direct, while the latter results from shielding effects.[9] The quadrupole splitting in noncubic complexes consists of a large (non-S-state atoms) ionic contribution, together with a contribution from ligands and lattice. In complexes with unfilled strong-octahedral-field shells (t_{2g} or e_g), the ionic contribution generally dominates lattice sources. There are also Sternheimer shielding and antishielding factors which affect the net efg, but these will be assumed constant in the present discussion.

Recent ME investigations by Wagner and coworkers have shown that in numerous octahedral complexes, in which the formal oxidation state of iridium varies between III (d^6) and IX (d^0), the isomer shift changes may be readily interpreted in terms of a loss of d electrons.[10,11] That is, the isomer shift exhibited a nearly linear increase with formal oxidation state of the metal ion, loss of one d electron corresponding to an increase in the isomer shift of roughly 1 mm/sec. It should be noted, however, that these authors also indicate the possible, though presently indeterminant, complication of σ-bonding changes among the compounds showing the monotonic variation in isomer shift and formal oxidation state.[10]

The substituted Cl-VA complexes, denoted Cl-VA–(XY), are qualitatively of two types. When the XY group is the O_2 molecule, it is found that a partial bond between oxygen atoms is retained.[12] In the other compounds studied the XY bond is broken, and the constituent species form bonds only with the central iridium atom. The former group is called type II and the latter type I.

Figure 1 shows that a correlation between isomer shift and ν_{CO} appears in type I compounds. The trend is of some interest since the change in isomer shift on going from the H_2 to the Cl_2 adduct indicates a decrease in s-electron density at the iridium nucleus. This is opposite to the shielding effect expected from simple d-electron loss. Since there is no direct way of determining the origin of this result, we only note here a plausible starting point for an interpretation of the data. All of the type I compounds are formally Ir(III) systems. It is therefore simplest to consider them as t_{2g}^6 con-

---

(7) L. Vaska and J. W. DiLazio, *J. Amer. Chem. Soc.*, **84**, 679 (1962).

(8) R. F. Heck, *ibid.*, **86**, 2796 (1964).

(9) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Lett.*, **6**, 98 (1961).

(10) F. Wagner and U. Zahn, *Z. Phys.*, **233**, 1 (1970).

(11) P. Rother, F. Wagner, and U. Zahn, *Radiochim. Acta*, **11**, 203 (1969).

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

figurations and ascribe variations in isomer shift to bonding changes in the t_{2g} orbitals and variations in d^2sp^3 hybrid populations owing to σ bonding. This procedure is consistent with experience in low-spin Fe(II) complexes.[13]

Changes in the iridium–ligand wave function will mainly depend on the surrounding neighbor ligands. When π acceptors are present, back-donation from the metal to the ligand may occur. Likewise, when σ donors are present, a ligand donation to the metal is a possibility. In both cases the effect is to increase the net s-electron density at the iridium nucleus: in the former process because of shielding and in the latter by direct s donation into d^2sp^3 type orbitals. Perhaps the best example of such a situation involves metal cyanide ligands.[14] The $K_3[Ir^{III}Cl_6]$ complex fits in nicely with the trends of Wagner, *et al.*,[10,11] but these authors note that $K_3[Ir^{III}(CN)_6]$ shows rather different behavior, owing to the π-acceptor nature of the cyanides. For $K_3[IrCl_6]$ the shift is -0.17 cm/sec and for $K_3[Ir(CN)_6]$ it is $+0.082$ cm/sec. The difference is 0.25 cm/sec and for two such acceptor adducts an approximate shift of $+0.08$ cm/sec is implied.

There are no cyano adducts among the compounds reported here, but it is empirically observed that the H^- ligand acts as a σ donor and produces shifts in $3d^6$ low-spin Fe(II) compounds that are at least as large as those due to CN^-.[13] This implies an approximate range of 0.1 cm/sec for the effects of ligand donor or acceptor properties in Vaska adducts. The data in Figure 1 are in agreement with this estimate. The loss of an electron density on going from Cl-VA–H_2 to Cl-VA–Cl_2 therefore becomes explicable in terms of the fact that the H^- ligand represents a much stronger σ donor than Cl^-. The intermediate adducts are also consistent with their relative powers as σ donors.[13,15]

The implication of σ donation for variations in the carbonyl stretch frequencies is less direct. The data show a decrease in ν_{CO} as the s-electron density increases. This suggests that increased shielding of t_{2g} electrons by s electrons can allow an expansion of the former into carbonyl π^* orbitals. This would result in decreased stretching frequencies.

The complication of σ and π effects is further illustrated by the Cl-VA–O_2 compound. Here a relatively small isomer shift is observed, though a substantial decrease in ν_{CO} occurs (both shifts relative to Cl-Vask–Cl_2). Finally we note that the two planar systems Cl-VA and Br-VA, formally $t_{2g}{}^6e_g{}^2$ configurations, do not show substantially decreased s-electron densities relative to Cl-VA–Cl_2. It seems likely that the presence of the 5d electrons in axial orbitals produces a relatively weak screening of the bonding s-type electrons which reside primarily in planar orbitals.

Acknowledgment.—It is a pleasure to acknowledge useful conversations with A. P. Ginsberg, R. L. Martin, and G. K. Wertheim.

---

(13) J. Danon in "Chemical Applications of Mössbauer Spectroscopy," V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, p 159.

(14) R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).

(15) G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc. A*, 956 (1970).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BALL STATE UNIVERSITY, MUNCIE, INDIANA 47306

The Synthesis of Phthalocyaninogermanium(II)[1]

BY RICHARD L. STOVER, CARY L. THRALL,
AND RALPH D. JOYNER*

Received December 23, 1970

Previous work with phthalocyaninogermanium complexes has included germanium(IV) compounds,[2–5] but the germanium(II) compound has not been described in the literature. Both phthalocyaninotin(IV) and phthalocyaninotin(II) compounds have been known for some time, and phthalocyaninolead(II) is the only lead phthalocyanine known.[6,7] This report concerns the synthesis and characterization of phthalocyaninogermanium(II).

An analytical method developed by Elvidge[8] was used to confirm the oxidation state of germanium. In this method a metal phthalocyanine consumes 2 equiv of oxidizing agent/mol if the central metal is not also oxidized. Additional ozidizing agent is needed if the central metal is in a low oxidation state and can be oxidized to a higher state.

Experimental Section

Reduction of Dichloro(phthalocyanino)germanium(IV)(PcGeCl_2)[9] with Sodium Borohydride.—A mixture of 0.80 g of PcGeCl_2 (0.0012 mol) and 0.14 g of sodium borohydride (0.0037 mol) was stirred at reflux (164–166°) in a mixture of 20 ml of benzyl alcohol and 10 ml of anisole for 1 hr. The mixture was filtered hot (medium-fritted glass Büchner), and the filtrate was allowed to stand for 2 days at room temperature. The cooled filtrate was again filtered (medium-fritted glass Büchner), and the solid residue was successively washed with water, dilute hydrochloric acid, water, and acetone. The oven-dried (110°) product weighed 0.55 g for a 78% yield of PcGe based on PcGeCl_2.

Purification was effected by heating a 490-mg sample in a vacuum sublimator at 450° for 30 min, under a pressure of 1–2 μ. The collecting finger of the sublimator was maintained at 357° by boiling mercury. A yield of 164 mg of β-PcGe crystals was obtained. The crystals were blue-green by transmitted light and had a reddish reflex. *Anal.* Calcd for $C_{32}H_{16}N_8Ge$: C, 65.69; H, 2.76; Ge, 12.41. Found: C, 65.86; H, 2.91; Ge, 12.63.[10]

Reduction of PcGeCl_2 with Sodium Borodeuteride.—Reaction of PcGeCl_2 with $NaBD_4$ in dry quinoline followed by sublimation gave a compound with an infrared spectrum identical with that of β-PcGe.

Reduction of PcGeCl_2 with Anhydrous Stannous Chloride.—A mixture of 3.0 g of PcGeCl_2 (0.0046 mol) and 3.0 g of $SnCl_2$ (0.016 mol) in 100 ml of dry quinoline was refluxed under nitrogen for 4 hr. The resulting mixture was allowed to cool and then filtered (medium-fritted glass Büchner) and washed with benzene, methanol, and ether. After air-drying, the product weighed 0.93 g. A second batch of product weighing 0.40 g for

---

[1] This research was supported in part by a grant from Research Corp. The work was reported in part at the Indiana Academy of Science Fall Meeting at Ball State University, Oct 1968, and at Indiana State University, Nov 1970.

(2) R. D. Joyner and M. E. Kenney, *J. Amer. Chem. Soc.*, **82**, 5790 (1960).

(3) R. D. Joyner, R. G. Linck, J. N. Esposito, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **24**, 299 (1962).

(4) A. J. Starshak, R. D. Joyner, and M. E. Kenney, *Inorg. Chem.*, **5**, 330 (1966).

(5) J. N. Esposito, L. E. Sutton, and M. E. Kenney, *ibid.*, **6**, 1116 (1967).

(6) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

(7) W. J. Kroenke and M. E. Kenney, *Inorg. Chem.*, **3**, 251 (1964).

(8) J. A. Elvidge, *J. Chem. Soc.*, 869 (1961).

(9) Pc = $C_{32}H_{16}N_8$, the phthalocyanino ligand.

(10) Galbraith Laboratories, Inc., Knoxville, Tenn.