

Figure 4. Ligand field splittings θ and Δ for octahedral complexes of the type $(\text{NEt}_4)_2\text{PaX}_6$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$).

to be split as in the spectra of other octahedral protactinium(IV) complexes^{1,2} and a range of uranium(V) complexes.^{12,13}

The assignments at 85 K shown in Table III were used to fit the ligand field splittings, θ and Δ , and the spin-orbit coupling constant, ζ , and in order to have a check on these parameters the g value for PaI_6^{2-} was estimated at -1.15 (cf. ref 1 and 2). The experimental and calculated values are compared in Table IV, and the θ and Δ values are compared with those for other hexahalogenoprotactinates(IV) in Figure 4. The apparent increase in the spin-orbit coupling constant ζ through the series from the fluoride to the iodide complex should be treated with caution since the values obtained are strongly dependent on the g values estimated. Magnetic measurements are necessary on these compounds in order to determine accurate values of ζ .

The very marked decrease in θ and the relatively constant value of Δ across the series $\text{PaF}_6^{2-} \rightarrow \text{PaI}_6^{2-}$ (Figure 4) reflect the progressive lowering in energy of the Γ_6 state relative to the Γ_8' and Γ_7' states shown in Table IV. The Γ_7' state in fact increases very slightly in energy from PaCl_6^{2-} to PaI_6^{2-} . As discussed previously, it can be shown for $5f^1$ compounds in octahedral symmetry that

$$\theta \approx (\alpha_\pi^2 + \alpha_\sigma^2 - \alpha_\pi'^2)(E_f - E_p) \quad (1a)$$

and

$$\Delta \approx (\alpha_\pi'^2)(E_f - E_p) \quad (1b)$$

where α_π and α_σ are ligand admixture coefficients for the t_{1u}

state, α_π' is that for the t_{2u} state, and E_f and E_p are the binding energies of the outer f metal ion electrons and the outer p shell ligand electrons, respectively. Thus, since θ changes much more rapidly than Δ for the hexahalogenoprotactinates(IV) (Figure 4) and α_π and α_π' involve the same ligand orbital, changes in π bonding will have relatively little effect on θ but (eq 1) will directly affect Δ . It appears therefore that as the halide ion is changed from fluoride to iodide in the hexahalogenoprotactinates(IV) $(\text{NEt}_4)_2\text{PaX}_6$ ($X = \text{F}-\text{I}$), large changes in σ bonding occur while the π bonding is relatively unaffected.

Summary

The preparation of actinide(IV)-hexaiodo complexes $\text{R}_2\text{M}^{\text{IV}}\text{I}_6$ ($\text{R} = \text{NEt}_4, \text{NMe}_3\text{Ph}$; $\text{M}^{\text{IV}} = \text{Th}, \text{Pa}, \text{U}$) is described. Ir, Raman, and electronic spectral data are reported for the protactinium(IV) and uranium(IV) complexes. Ligand field parameters and spin-orbit coupling constants derived for the hexaiodoprotactinates(IV) are discussed in relationship to earlier values obtained for other octahedral hexahalogenoprotactinates(IV), $(\text{NEt}_4)_2\text{PaX}_6$ ($X = \text{F}, \text{Cl}, \text{Br}$), and shown to fit the trends previously identified for these compounds.

Registry No. $(\text{NEt}_4)_2\text{ThI}_6$, 56848-01-2; $(\text{NEt}_4)_2\text{PaI}_6$, 56930-81-5; $(\text{NEt}_4)_2\text{UI}_6$, 56848-06-7; $(\text{NMe}_3\text{Ph})_2\text{PaI}_6$, 51268-19-0; $(\text{NMe}_3\text{Ph})_2\text{UI}_6$, 58002-46-3.

References and Notes

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Anionic Linear Chain Iridium Carbonyl Halides

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The compounds $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$, $(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$ ($\text{TTF} = \text{tetrathiafulvalenium}$), $\text{K}_{0.57}\text{Ir}(\text{CO})_2\text{Br}_2 \cdot 0.2\text{C}_6\text{H}_5\text{COCH}_3$, and $\text{Cs}_{0.60}\text{Ir}(\text{CO})_2\text{Br}_2$ have been investigated by chemical analysis, infrared and ^{193}Ir Mössbauer spectroscopy, electrical conductivity, and magnetic susceptibility measurements. Conducting linear chains of $\text{cis}[\text{Ir}(\text{CO})_2\text{X}_2]^{0.60-}$ ($X = \text{Cl}, \text{Br}$) units are shown to be present in these compounds. The apparently well-defined compounds $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42} \cdot 0.2\text{CH}_3\text{COCH}_3$ and $\text{Na}_{0.93}\text{Ir}(\text{CO})_2\text{Cl}_{2.32} \cdot 0.3\text{CH}_3\text{COCH}_3$ are reformulated as $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2 \cdot 0.4\text{KCl} \cdot 0.2\text{CH}_3\text{COCH}_3$ and $\text{Na}_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2 \cdot 0.32\text{NaCl} \cdot 0.3\text{CH}_3\text{COCH}_3$, in which the KCl and NaCl are present interstitially in the lattice of linear chains.

Square-planar coordinated transition metal atoms often stack along the axis perpendicular to the ligand planes to form linear chains of metal-metal bonded atoms. A compound made up of parallel chains of this type, with only weak in-

teraction between adjacent chains, is a potential one-dimensional conductor. In order for such a compound to be highly conducting, the d -band arising from the metal-metal interaction must not be completely filled. The known

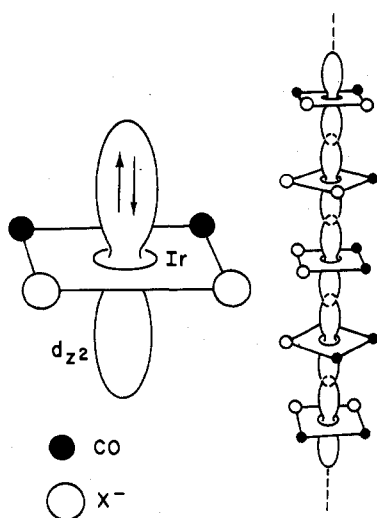


Figure 1. Linear-chain structure of $[\text{Ir}(\text{CO})_2\text{X}_2]^{0.6-}$ ($\text{X} = \text{Cl}, \text{Br}$) showing overlap of d_{z^2} orbitals.

examples¹ contain either $\text{Pt}(2+)$ or $\text{Ir}(1+)$ and the required holes in the d band are introduced by partial oxidation of the metal ions. The degree of partial oxidation determines the number of charge carriers per metal atom. Thus, the extensively studied compound $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}\cdot 3\text{H}_2\text{O}$ has three carriers for every ten Pt atoms, while in $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$ there is one carrier per ten Ir atoms.

Since conductivity is proportional, among other things, to the density of charge carriers, materials with a high degree of partial oxidation might show enhanced conductivity. This possibility prompted us to investigate the compounds of reported stoichiometry $\text{M}[\text{Ir}(\text{CO})_2\text{Cl}_{2.4}]$ ($\text{M} = \text{K}, \text{Na}$)² and $\text{K}_{0.5}[\text{Ir}(\text{CO})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$).^{2,3} The anionic complexes in these compounds have been formulated as halogen-bridged dimers² and as square-planar $[\text{Ir}_4(\text{CO})_8\text{X}_8]^{2-}$ clusters held together by Ir-Ir bonds,³ analogous to the known structure of the diamagnetic ion $[\text{Re}_4(\text{CO})_{16}]^{2-}$. However, their appearance (hairlike needles with a bronze luster) and a report⁴ that $\text{K}_{0.5}[\text{Ir}(\text{CO})_2\text{Cl}_2]$ and " $\text{K}[\text{Ir}(\text{CO})_2\text{Cl}_{2.5}]$ " are highly conducting suggest a linear chain structure.⁵ In this paper we present a study of the stoichiometry, conductivity, ¹⁹³Ir Mossbauer spectra, magnetic susceptibility, and infrared vibrational spectra, as well as the preparation of a cesium and a tetrathiofulvalenium (TTF) salt. A separate paper⁷ describes the nonvibrational ir and uv visible spectra.

Our results show that the compounds all contain linear chains of square-planar *cis*- $[\text{Ir}(\text{CO})_2\text{X}_2]^{0.6-}$ ($\text{X} = \text{Cl}, \text{Br}$) units, as illustrated in Figure 1. The temperature dependence of the powder conductivities is consistent with one-dimensional hopping between localized states. That the charge carriers are not localized to individual atoms is shown by the Mossbauer spectra, which consist of a quadrupole split doublet with an isomer shift intermediate between the values found for iridium(I) and iridium(II) carbonyl chlorides. The presence of only a small Curie component in the magnetic susceptibility confirms the absence of significant amounts of discrete iridium(II) in the chains.

Results

Optical Microscopy. The compounds formed as clumps of interlaced fibers comprised of many parallel needles. The needles are dichroic, transmitting red-brown for light vibrating parallel to the long dimension and pale yellow for the transverse direction; they have a metallic copper luster in reflected light. In a few instances, fibers approaching 1 cm in length were obtained.

Stoichiometry. Table I summarizes the analytical results.

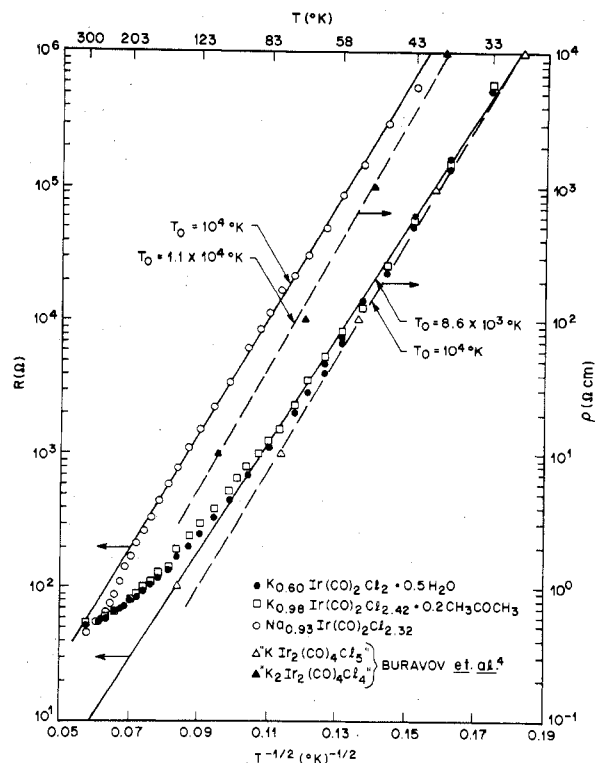


Figure 2. Temperature dependence of the resistance of compressed polycrystalline potassium and sodium salts of $[\text{Ir}(\text{CO})_2\text{Cl}_2]^{0.6-}$.

Halogen:Ir and cation:Ir (S:Ir in the case of the TTF salt) ratios are given for each sample analyzed; the percentage composition is the mean for all the samples of each compound. At least two independent preparations were analyzed, except in the case of the sodium salt where only a single sample was examined. The stoichiometry of the nominal $\text{KIr}(\text{CO})_2\text{Cl}_{2.5}$ agrees with the original formulation, $\text{K}_2\text{Ir}_2(\text{CO})_4\text{Cl}_{4.8}$.² Analyses of the nominal $\text{K}_{0.5}\text{Ir}(\text{CO})_2\text{Cl}_2$ give K:Ir = 0.60 ± 0.02 , in agreement with the recent result of Krogmann and Geserich⁶ and in disagreement with the original formulation as $\text{KIr}_2(\text{CO})_4\text{Cl}_4$. The Cs^+ and TTF^+ salts are reported here for the first time.

Infrared CO and IrCl Stretching Frequencies. These are summarized in Table II. The CO stretching frequencies of " $\text{K}_2[\text{Ir}_4(\text{CO})_8\text{Cl}_8]$ ", as reported by Cleare and Griffith,³ agree with the results for $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.5\text{H}_2\text{O}$.

Electrical Conductivity. The temperature dependence of the resistance of the sodium- and the two potassium-chloro salts is shown in Figure 2, while Figure 3 shows the results for the TTF salt. The solid and dashed lines in the figures are plots of the relation

$$R = R_0 \exp(T_0/T)^{1/2} \quad (1)$$

for the indicated value of T_0 . The measurements are well fitted by this relation over most of the range of $T^{-1/2}$ values studied. $\text{Cs}_{0.60}\text{Ir}(\text{CO})_2\text{Br}_2$ and $\text{K}_{0.57}\text{Ir}(\text{CO})_2\text{Br}_2$ have a similar temperature dependence. Table III lists for each compound the room-temperature resistance, the temperature range over which relation 1 is obeyed, and the value of the exponent T_0 . The geometry used in the electrical measurements corresponded to the resistivity in ohm-cm being approximately equal to one-third of the resistance. The relation is only approximate because the length of the powder samples varied from run to run.

Buravov et al.⁴ have measured the temperature dependence of the resistivity of " $\text{K}_2\text{Ir}_2(\text{CO})_4\text{Cl}_5$ " and " $\text{KIr}_2(\text{CO})_4\text{Cl}_4$ ". They reported an almost exponential decrease in conductivity

Table I. Analytical Results for Salts of Anionic Iridium Carbonyl Halides

Nominal stoichiometry	Sample	Found		Assigned stoichiometry	% Ir		% X		% M		% C		% H	
		X ^a :Ir	M ^b :Ir		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
KIr(CO) ₂ Cl _{2.5}	I	2.45	0.99	K _{0.98} Ir(CO) ₂ Cl _{2.42} ·0.2CH ₃ COCH ₃	50.06	50.02	22.35	22.30	9.98	9.96	8.13	7.56	0.31	0.32
	II	2.42	0.98		52.04	51.57	22.28	22.11	5.79	5.76	9.43	8.24	0.49	0.75
	III	2.38	0.96		54.26	54.35	20.02	19.59	6.62	6.26	8.82	8.30	0.34	0.55
	Mean	2.42 ± 0.02	0.98 ± 0.01		54.66	54.75	20.17	19.94	6.67	6.72	6.83	7.02	0.29	0.22
NaIr(CO) ₂ Cl _{2.5}	I	1.95	0.57	Na _{0.93} Ir(CO) ₂ Cl _{2.32} ·0.3CH ₃ COCH ₃	43.49	43.70	36.16	36.09	5.04	5.04	7.06	7.59	0.27	0.47
	II	1.95	0.57		39.40	39.67	32.76	32.72	16.35	16.46	4.92	0		
	III	1.95	0.59		43.31	42.86	15.98	15.50	17.63	17.32	15.32	15.43	0.55	0.62
	Mean	1.97 ± 0.02	0.60 ± 0.02		(TTF) _{0.61} Ir(CO) ₂ Cl ₂									
K _{0.5} Ir(CO) ₂ Br ₂	I	1.95	0.56	C _{8.60} Ir(CO) ₂ Br ₂ ·0.2CH ₃ COCH ₃	43.49	43.70	36.16	36.09	5.04	5.04	7.06	7.59	0.27	0.47
	II	2.00	0.54		39.40	39.67	32.76	32.72	16.35	16.46	4.92	0		
	III	2.01	0.60		43.31	42.86	15.98	15.50	17.63	17.32	15.32	15.43	0.55	0.62
	Mean	1.99 ± 0.02	0.57 ± 0.02		(TTF) _{0.61} Ir(CO) ₂ Cl ₂									
C _{8.5} Ir(CO) ₂ Br ₂	I	1.98	0.59	C _{8.5} Ir(CO) ₂ Br ₂	43.49	43.70	36.16	36.09	5.04	5.04	7.06	7.59	0.27	0.47
	II	1.96	0.59		39.40	39.67	32.76	32.72	16.35	16.46	4.92	0		
	III	2.01	0.62		43.31	42.86	15.98	15.50	17.63	17.32	15.32	15.43	0.55	0.62
	Mean	1.98 ± 0.02	0.60 ± 0.01		(TTF) _{0.61} Ir(CO) ₂ Cl ₂									
(TTF) _{0.5} Ir(CO) ₂ Cl ₂	I	1.96	2.36	(TTF) _{0.61} Ir(CO) ₂ Cl ₂	43.31	42.86	15.98	15.50	17.63	17.32	15.32	15.43	0.55	0.62
	II	2.47	2.47											
Mean		2.42 ± 0.06												

^a X = Cl or Br. ^b M = Na, K, Cs, or S in the TTF salt. ^c TTF = C₈H₈S₄, 1,4,5,8-tetrahydro-1,4,5,8-tetrathiafulvalene. ^d Product recrystallized from acetone; only one sample of this type was analyzed.

Table II. Infrared CO and IrX (X = Cl, Br) Stretching Frequencies for Salts of Anionic Iridium Carbonyl Halides

Compd	$\nu(\text{CO})$, ^{a,b} cm ⁻¹	$\nu(\text{IrCl})$, ^{b,c} cm ⁻¹
K _{0.98} Ir(CO) ₂ Cl _{2.42} ·0.2-CH ₃ COCH ₃	2039 s, 2080 m, 2110 w	320 m, 300 m, 280 sh
	1965 s, 2043 ms	
K _{0.98} Ir(CO) ₂ Cl _{2.42} ·0.5H ₂ O	2040 s, 2080 m, 2115 w	317 m, 300 m, 280 sh
	2028, 2070	320 m, 305 m, 280 sh
C _{8.60} Ir(CO) ₂ Br ₂	2020, 2065, ~2100 sh	

^a In Nujol or Fluorolube mulls unless otherwise indicated. ^b Key: sh, shoulder; s, strong; m, medium; w, weak. ^c In Nujol mulls. ^d In acetone solution.

Table III. Temperature Dependence of the Resistance of Salts of Anionic Iridium Carbonyl Halides

Compd	R(300 K), ^a Ω	T ₀ , K	Temp range (K) over which eq 1 is obeyed
K _{0.98} Ir(CO) ₂ Cl _{2.42} ·0.2CH ₃ ·COCH ₃ ^b	100	10 ⁴	140–33
K _{0.98} Ir(CO) ₂ Cl _{2.42} ·0.2CH ₃ ·COCH ₃ ^b	54	8.6 × 10 ³	100–33
K _{0.60} Ir(CO) ₂ Cl ₂ ·0.5H ₂ O ^b	50	8.6 × 10 ³	100–33
K _{0.60} Ir(CO) ₂ Cl ₂ ·0.5H ₂ O ^b	21	6.3 × 10 ³	110–33
Na _{0.93} Ir(CO) ₂ Cl _{2.32}	45	1.0 × 10 ⁴	160–43
(TTF) _{0.61} Ir(CO) ₂ Cl ₂	190	1.0 × 10 ⁴	300–43
K _{0.57} Ir(CO) ₂ Br ₂ ·0.2CH ₃ COCH ₃	20	1.0 × 10 ⁴	100–33
C _{8.60} Ir(CO) ₂ Br ₂ ^b	31	1.2 × 10 ⁴	180–33
C _{8.60} Ir(CO) ₂ Br ₂ ^b	42	8.6 × 10 ³	300–33

^a ρ ≈ 1/3R; see discussion in text. ^b Samples from two independent preparations were measured.

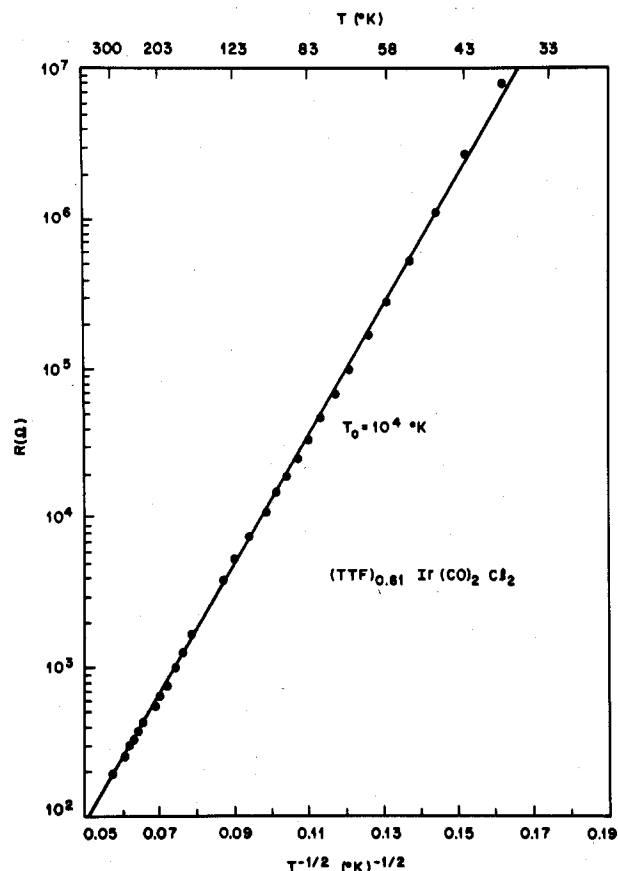


Figure 3. Temperature dependence of the resistance of compressed polycrystalline $(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$.

Table IV. Mössbauer Parameters from Least Squares Analysis of Spectra of Iridium Carbonyl Halides

Compd	Isomer shift, ^{a,b} mm/s	Quadrupole splitting, ^b mm/s
$\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}\cdot 0.2\text{CH}_3\text{COCH}_3$	-0.0839 ± 0.005	3.54 ± 0.01
$\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.5\text{H}_2\text{O}$	-0.088 ± 0.006	3.776 ± 0.01
$\text{Na}_{0.93}\text{Ir}(\text{CO})_2\text{Cl}_{2.32}$	-0.116 ± 0.011	3.874 ± 0.022
$(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$	-0.088 ± 0.006	3.998 ± 0.012
$\text{K}_{0.57}\text{Ir}(\text{CO})_2\text{Br}_2$	-0.164 ± 0.007	3.99 ± 0.007
$\text{Cs}_{0.60}\text{Ir}(\text{CO})_2\text{Br}_2$	-0.154 ± 0.01	3.732 ± 0.01
$(\text{Ph}_4\text{As})\text{Ir}(\text{CO})_2\text{Cl}_2$	$+0.063 \pm 0.013$	5.472 ± 0.026
$(\text{Ph}_4\text{As})_2\text{Ir}_2(\text{CO})_4\text{Cl}_6$	-0.228 ± 0.024	1.888 ± 0.042
$\text{Ir}(\text{CO})_3\text{Cl}_{1.1}^b$	-0.04 ± 0.007	2.06 ± 0.013

^a With respect to iridium metal. ^b Uncertainties are standard errors.

with decreasing temperature. We have replotted their data in Figure 2 to show their measurements to be in good agreement with the temperature dependence of relation 1 for $T_0 = 10^4$ K, a value similar to those found in our measurements (Table III).

Mössbauer Spectroscopy. Mössbauer spectra were obtained at 4.2 K for all of the compounds in Table I, as well as for the square-planar Ir(1+) complex $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$ and the halogen-bridged Ir(2+) dimer $[\text{Ir}_2(\text{CO})_4\text{Cl}_6]^{2-}$. Analysis of the data was as described previously.⁸ Table IV summarizes the results and, for comparison, shows the parameters for $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$.⁸ Figure 4 shows the fit for the spectrum of $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.5\text{H}_2\text{O}$. This is typical of the spectra of the alkali metal and TTF salts: two independent lines of equal intensity are required for the fit and these are identified as the components of a quadrupole split doublet.

The fit of the calculated to the observed spectra was in all cases sufficiently good that a significant improvement could not be obtained by introducing additional lines into the

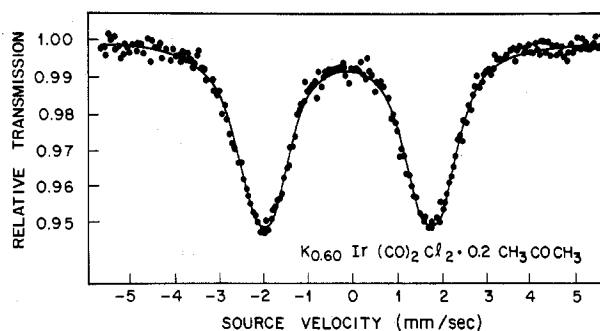


Figure 4. Mössbauer spectrum and least-squares fit for $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.2\text{CH}_3\text{COCH}_3$.

Table V. Curie Component of the Magnetic Susceptibility of Iridium Carbonyl Halides

Compd	$\mu_{\text{eff}}(4.4\text{--}300\text{ K})$, ^a BM	
	Sample I	Sample II
$\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}\cdot 0.2\text{CH}_3\text{COCH}_3$	0.05	0.28
$\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.5\text{H}_2\text{O}$	0.17	
$(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$	0.35	0.02

^a Calculated from the slope of a χ_A' vs. $1/T$ plot in the range 4.4–300 K.

analysis. The line widths determined from the least-squares fits were in the range 0.94–1.18 mm/s and are consistent with those obtained from measurements with an iridium metal absorber. They arise from the natural line width (0.6 mm/s) plus small additional contributions from source inhomogeneities and absorber thickness (saturation) broadening. Similar line widths were obtained for $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$.

Magnetic Susceptibility. Measurements were carried out on $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}\cdot 0.2\text{CH}_3\text{COCH}_3$, $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.5\text{H}_2\text{O}$, and $(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$. All of the samples contained small amounts of saturated ferromagnetic impurity, as evidenced by the field dependence of the room-temperature susceptibility. The susceptibilities obeyed the Curie law from 4.4 to 300 K; Table V gives the values of μ_{eff} determined from the slopes of plots of the molar susceptibility against $1/T$.

Discussion

The analytical results in Table I show that the oxidation state of iridium in the anionic complexes is in the range 1.39–1.44. This corresponds to 3.9–4.4 charge carriers for every ten Ir atoms, significantly more than in the partially oxidized platinum cyanide complexes or in $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$. The cation-deficient partial oxidation demonstrated in Table I is reminiscent of what has been found for platinum bis(oxalate) complexes; for example, in the latter system the salts $\text{Na}_{1.67}\text{Pt}(\text{C}_2\text{O}_4)_4\cdot 4\text{H}_2\text{O}$ and $\text{K}_{1.62}\text{Pt}(\text{C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O}$ are known.⁹

Equation 1 has been found to describe the temperature dependence of the resistance of a number of linear-chain conductors and has been taken as evidence for one-dimensional hopping conductivity between localized states.^{10–12} Except for very low temperatures, where the resistance is nonohmic, and high temperatures, where the hopping model no longer applies, eq 1 is in agreement with the measured temperature dependence of the resistance for the compounds in Table I. Furthermore, the values of the exponent T_0 ($\approx 10^4$ K) which are summarized in Table III, are quite close in magnitude to those reported for several one-dimensional conductors (e.g., for $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}\cdot 3\text{H}_2\text{O}$, $T_0 = 1.06 \times 10^4$ K and for $\text{Mg}_{0.82}\text{Pt}(\text{C}_2\text{O}_4)_2\cdot 5.3\text{H}_2\text{O}$, $T_0 = 7.20 \times 10^3$ K).¹¹ It is clear from Table III that variation of the cation (Na^+ , K^+ , Cs^+ , TTF^+) or the anionic ligand (Cl^- , Br^-) does not have a large effect on the electrical resistivity or on T_0 . The conductivity behavior just described, taken together with the morphological

and optical anisotropy (dichroism) of the compounds, is strong evidence that they are linear-chain conductors.

Information concerning the ligand coordination geometry about the Ir atoms is provided by the infrared CO and IrCl stretching frequencies (Table II). Two terminal CO stretching frequencies are found for the TTF salt in the solid state; all of the other compounds have three $\nu(\text{CO})$ vibrations. $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}$ in solution shows only two $\nu(\text{CO})$ vibrations instead of three as in the solid state. The solid-state spectra of the chloro complexes have two bands and a shoulder in the IrCl stretching region. An isolated *cis*- $\text{Ir}(\text{CO})_2\text{Cl}_2$ unit is expected to have two ir-active $\nu(\text{CO})$ and two ir-active $\nu(\text{IrCl})$ frequencies, while an isolated *trans*- $\text{Ir}(\text{CO})_2\text{Cl}_2$ will have one ir-active $\nu(\text{CO})$ and one ir-active $\nu(\text{IrCl})$ frequency. The CO stretching region spectrum of the TTF salt and the solution spectrum of $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}$ are clearly consistent with *cis* coordination. The spectra of the other compounds are also consistent with *cis* coordination if we make the reasonable assumption that the third, weak, CO band and the IrCl shoulder arise from a solid-state interaction. We therefore believe that all of these compounds have *cis* ligand geometry in the linear-chain structure illustrated in Figure 1.

All of the compounds studied have very similar Mössbauer spectra (Figure 4 and Table IV): in each case there is a single Mössbauer resonance that appears as a doublet because of quadrupole splitting of the $I = 3/2$ ^{193}Ir nuclear ground state. Since the complexes all have ^1A electronic ground states, the splitting must arise from interaction of the nuclear quadrupole moment with the field gradient due to the ligands, as shielded by the Sternheimer factor. A rough estimate of the ligand field gradient may be obtained by considering the chloride ligands to be point charges of $-e$ disposed at the corners of a square of diagonal 4.8 Å with neutral CO groups at the remaining corners and Ir at the center of the square. Using a value of $Q = 1.5$ bohrs for the Ir nuclear moment¹³ and estimating a Sternheimer factor of $\gamma_\infty = -70$ for Ir^+ ,¹⁴ a quadrupole splitting of 4.5 mm/s is obtained for both $[\text{Ir}(\text{CO})_3\text{Cl}]$ and $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$. The actual non-point-charge character of the Cl^- will tend to reduce the field gradients and therefore the quadrupole splittings. These simple estimates suggest that the ligand field gradients alone can account for the observed quadrupole splittings.

The occurrence of only a single Mössbauer doublet for each compound indicates that all of the Ir atoms in the chain are equivalent and argues against there being more than one coordination geometry in the chain, e.g., alternating $\text{Ir}(\text{CO})_3\text{Cl}-\text{Ir}(\text{CO})\text{Cl}_3$ or alternating *cis*- $\text{Ir}(\text{CO})_2\text{Cl}_2$ -*trans*- $\text{Ir}(\text{CO})_2\text{Cl}_2$ units. This supports the interpretation of the infrared spectra. Furthermore, as in $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$,⁸ we can conclude that the charges (holes) arising from partial oxidation of $\text{Ir}(\text{CO})_2\text{Cl}_2^-$ units are not localized to individual iridium atoms but must be delocalized over some segment of the iridium chain, possibly by rapid hopping between iridium atoms in different oxidation states. The spectra would only be consistent with hopping time faster than $\sim 10^{-10}$ s at 4.2 K. Localization of the charges to individual atoms could produce $\text{Ir}(2+)$ or $\text{Ir}(3+)$; to account for the stoichiometry 40% $\text{Ir}(2+)$ or 20% $\text{Ir}(3+)$ is required. Either of these would appear as an easily detected second doublet in the spectra if either the isomer shift or the quadrupole splitting were appreciably different from the values for $\text{Ir}(1+)$ units.

Comparison of the Mössbauer spectra of $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$, $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$, $[\text{Ir}(\text{CO})_2\text{Cl}_2]^{0.6-}$, and $[\text{Ir}_2(\text{CO})_4\text{Cl}_6]^{2-}$ leads to the following order of isomer shifts with oxidation states: $\text{Ir}(2+)$, -0.228 ; $\text{Ir}(1.4+)$, -0.116 to -0.084 ; $\text{Ir}(1.1+)$, -0.04 ; $\text{Ir}(1+)$, $+0.063$. The intermediate value of the isomer shift for the chain complexes, between the values for $\text{Ir}(1+)$ and $\text{Ir}(2+)$, is further evidence that the charge carriers are de-

localized and that the iridium atoms may be assigned non-integral oxidation states. The decrease in isomer shift with increase in oxidation state from $1+$ to $2+$ is opposite to what has been observed for complexes of the higher oxidation states of iridium. This inversion of the oxidation state dependence of the isomer shift is very unusual; we have discussed its significance in a separate publication.¹⁵

Since the infrared and Mössbauer spectra show that in the Na^+ , K^+ , Cs^+ , and TTF^+ salts the Ir atoms have the same coordination geometry, it is clear that in the compounds $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}\cdot 0.2\text{CH}_3\text{COCH}_3$ and $\text{Na}_{0.93}\text{Ir}(\text{CO})_2\text{Cl}_{2.32}$, part of the Cl^- is not coordinated to the iridium. These compounds are more correctly formulated as $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.4\text{KCl}\cdot 0.2\text{CH}_3\text{COCH}_3$ and $\text{Na}_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.32\text{NaCl}$. They are not simple mechanical mixtures of $\text{M}_{0.6}\text{Ir}(\text{CO})_2\text{Cl}_2$ with KCl or NaCl , since x-ray powder patterns show no evidence of lines due to crystalline KCl or NaCl . The latter are probably present as interstitial coprecipitates in the $\text{M}_{0.6}\text{Ir}(\text{CO})_2\text{Cl}_2$ lattice.

Material of composition $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2\cdot 0.33\text{KCl}\cdot 0.2\text{C}_2\text{H}_5\text{COCH}_3$ can be prepared by precipitating an acetone solution of $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$ that has been stirred with solid potassium chloride. On the other hand, crystallization of an aqueous solution of $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}$ or $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$ in the presence of excess KCl invariably gives $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$. A clue to understanding this behavior is the observation that acetone solutions of $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}$ concentrate to a dark green solution, from which the copper-colored product deposits, while acetone solutions of $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$ concentrate to a dark blue-purple solution which then deposits the copper-colored product. We suggest that in acetone solution chain fragments can weakly coordinate additional Cl^- , probably to the end atoms of the fragments, as terminal or bridging groups. In sufficiently concentrated solution long chains form and the product crystallizes, coprecipitating as KCl the "extra" chloride that has been displaced by metal-metal bond formation. The concentrated aqueous solution from which $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$ deposits is green, indicating that it contains the precursor with "extra" coordinated Cl^- . In this case, however, KCl does not coprecipitate simply because it is soluble in water.

The magnetic susceptibilities of the compounds studied (Table V) varied appreciably in different samples, presumably because of the presence of small but varying amounts of paramagnetic impurities or defects. We take the smallest μ_{eff} (4.4–300 K) of each compound to be an upper limit of the intrinsic Curie-type susceptibility. These results are similar to what was found for $\text{Ir}(\text{CO})_3\text{Cl}_{1.1}$ ($\mu_{\text{eff}} = 0.074\text{--}0.091 \text{ BM}$)⁸ and demonstrate the absence of significant amounts of $\text{Ir}(2+)$ in the temperature range studied. The very small value of μ_{eff} found for the second sample of $(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$ is particularly interesting. Since TTF^+ has an unpaired spin, it cannot be present in the salt as a simple monocation but must form clusters or linear stacks in which the spin is quenched. The possibility that the TTF is stacked and that the unpaired spins are delocalized along the stack is unlikely because of the very similar appearance (color, morphology, dichroism) and conductivity behavior of the TTF and the alkali metal salts of $[\text{Ir}(\text{CO})_2\text{Cl}_2]^{0.6-}$.

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques; solvents were distilled under nitrogen before use. The products were stored and handled in an argon-filled glovebox. C, H, and S microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Schwarzkopf Laboratory, Woodside, N.Y. Analyses for iridium, alkali metal, and halogen were carried out by us using the procedure described below. Infrared spectra were measured with a Perkin-Elmer 457 grating spectrophotometer. The 73-keV transition in ^{193}Ir ($1/2+ \rightarrow 3/2+$) was used for all of the Mössbauer experiments; spectra were measured as described

previously⁸ with both source and absorber at 4.2 K. The source γ ray was quadrupole split by 0.48 mm/s. Magnetic susceptibility measurements were made as described previously⁸ over the temperature range 4.4–300 K at 13 kOe. Field dependence was checked at each end of the temperature range by varying the field from 1 to 13 kOe.

Electrical resistance measurements were made on powders pressed in a phenol fiber cylinder between a fixed copper electrode and a pistonlike copper rod electrode. The powders were kept compressed during the measurements by tying the piston in position with a twisted tantalum wire. All samples were measured with a constant voltage of 1.5 V; the resulting current was measured on a Keithley 615 electrometer. The low voltage ensured ohmic results down to the lowest temperature (28 K).

Preparation of Complexes. $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}\cdot 0.2\text{CH}_3\text{COCH}_3$. Attempts to prepare this compound by the carbonylation of potassium hexachloroiridate(IV) with CO at 200 atm and 200 °C in the presence of copper as halogen acceptor, as described by Malatesta and Canziani,² were unsuccessful. However, the required complex was readily obtained by treating potassium hexachloroiridate(III) (2–5 g) with carbon monoxide at 75–100 atm and 215–232 °C for 20–40 h. The K_3IrCl_6 was contained between glass wool plugs in a glass tube with constricted ends. The glass tube was placed in a copper tube open at one end, and the latter was sealed in a stainless steel autoclave in which the reaction was carried out. The crude product was a gold-brown powder, with a mirrorlike copper-colored film on the walls of the glass tube. Each gram of crude product was extracted with 200 ml of acetone; after filtering, the complex was isolated either by stripping to a small volume or by precipitation with benzene followed by stripping to ca. one-fourth the total volume; yield 75–80%. Samples for analysis and physical measurements were dried at 56 °C (10^{-3} mm).

$\text{Na}_{0.93}\text{Ir}(\text{CO})_2\text{Cl}_{2.32}$. This compound was obtained by the carbonylation of sodium hexachloroiridate (III) as described above for the potassium salt.

$\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_{2.05}\cdot 0.5\text{H}_2\text{O}$. This complex was prepared in two ways. (a) The crude product from the carbonylation of potassium hexachloroiridate(III) (2.8 g) was dissolved in 0.2% hydrochloric acid (115 ml) at 50 °C to give a yellow solution. The latter was filtered, potassium chloride (15 g) was added to the filtrate, and after re-warming to 50 °C the solution was filtered again and then cooled in ice. After 8 h, the complex which had crystallized was collected by filtration, washed with ice water, and dried at 56 °C (10^{-3} mm). Additional crops of product were obtained by adding more potassium chloride (6 g) to the yellow filtrate from the first crop, cooling in ice, and filtering periodically over the next 4 days. A small amount of black precipitate was a contaminant in the product formed after the first day; total yield 1.02 g (54%). This procedure is a modification of the method reported by Malatesta and Canziani² to give $\text{K}_2\text{Ir}_2(\text{CO})_4\text{Cl}_4$. (b) The complex can also be prepared by a modification of the procedure reported by Cleare and Griffith³ to give $[\text{Ir}_4(\text{CO})_8\text{Cl}_8]^{2-}$. Potassium hexachloroiridate(IV) (2 g) was refluxed for 12 h with concentrated hydrochloric acid (10 ml) and 90% formic acid (10 ml) to give a gold crust on a small amount of yellow solution. The product was isolated by adding 24 ml of degassed water, reheating to reflux, and filtering to give a clear yellow solution that rapidly turns green. Potassium chloride (2 g) was added and after re-warming the solution was cooled in ice for 8 h. The product was collected by filtration, washed with cold water and dried at 56 °C (10^{-3} mm); yield 1.25 g (85%).

$(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$. A solution of $(\text{TTF})_3(\text{BF}_4)_2$ ¹⁶ (254 mg, 0.969 mmol of TTF) in hot acetone (270 ml) was filtered into a solution of $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_{2.05}\cdot 0.5\text{H}_2\text{O}$ (695 mg, 1.98 mg-atoms of Ir) in acetone (250 ml). A fluffy, copper-colored precipitate formed almost immediately. The solution was warmed to 50 °C and then cooled in ice overnight. The product was collected, washed thoroughly with water (75 ml) followed by a small amount of acetone, and then dried at 25 °C (10^{-3} mm); yield 358 mg (41% based on Ir).

$\text{K}_{0.57}\text{Ir}(\text{CO})_2\text{Br}_{2.0}\cdot 0.2\text{CH}_3\text{COCH}_3$. Decarbonylation of formic acid by potassium hexachloroiridate(IV) in the presence of hydrobromic acid, according to the procedure of Cleare and Griffith³ for the preparation of $\text{K}_2\text{Ir}_4(\text{CO})_8\text{Br}_8$, affords the complex. Potassium bromide (2 g) was added to the solution immediately before crystallization to improve the yield. The reaction was erratic and gave variable yields.

$\text{Cs}_{0.60}\text{Ir}(\text{CO})_2\text{Br}_2$. The cesium salt was obtained by adding cesium bromide (3 g) to the filtrate from the preparation of $\text{K}_{0.57}\text{Ir}(\text{CO})_2\text{Br}_2$;

it was washed with water and dried at 56 °C (10^{-3} mm).

Reaction of $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$ with Potassium Chloride. $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_{2.05}\cdot 0.5\text{H}_2\text{O}$ (249 mg, 0.708 mmol) and potassium chloride (153 mg, 2.05 mmol) were ground together in an agate mortar. The mixture was stirred with acetone (100 ml) for 15 min; during this time the initially purple solution changed to red and then to light orange. Undissolved KCl was filtered off and benzene (100 ml) was added to the solution which was then concentrated (25 °C (10^{-2} mm)) to half its volume. The fluffy copper-colored product was collected, washed with 10% acetone–benzene, and dried at 56 °C (10^{-3} mm); yield 175 mg (65%). Anal. Calcd for $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_{2.0}\cdot 0.33\text{KCl}\cdot 0.25\text{CH}_3\text{COCH}_3$: K, 9.53; Cl, 21.64; Ir, 50.35. Found: K, 9.57; Cl, 21.69; Ir, 50.38.

Analysis for Alkali Metal, Iridium, and Halogen. Malatesta and Canziani² decomposed their potassium iridium carbonyl halide complexes by slowly heating them to 1000 °C in a stream of dry hydrogen. The samples were contained in a platinum boat enclosed in a 10 mm wide quartz tube; iridium metal remained in the boat as residue, and potassium distilled to the colder parts of the tube as the halide while the remaining halogen was evolved as hydrogen halide and was absorbed in water through which the effluent gases passed. Alkali metal, total halogen, and iridium can therefore be determined on a single sample. In our hands, the procedure as described by Malatesta and Canziani gave poor reproducibility and low results on samples of the chloro complexes. We associate this with the etching of the quartz tube in the hot zone, observed after each run. The difficulty was overcome by placing the boat containing the sample (50–70 mg) inside an 8-mm i.d. \times 170 mm long platinum tube; the latter was contained in a 24-mm i.d. \times 500 mm long quartz tube and was centered in a furnace with an 84 mm long hot zone. A quartz-enclosed thermocouple, centered in the hot zone just above the platinum tube and within the quartz tube, was used to measure the temperature. With this modification, etching of the quartz did not occur and good reproducibility was obtained in duplicate analyses. The effluent gases were passed through a trap containing a known excess of acidified standard 0.1 N silver nitrate followed by a trap containing plain water. Chloride absorbed in the traps was determined by a Volhard titration on the combined contents. By running blanks with potassium chloride, it was found that a small amount of KCl was carried over into the traps instead of condensing in the tube. The amount carried over depended on the hydrogen flow rate; under the conditions we used (70 cm³/min) 0.94% of the potassium chloride appeared in the traps. This correction was applied to all titrations of condensed KCl.

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Registry No. $\text{K}_{0.98}\text{Ir}(\text{CO})_2\text{Cl}_{2.42}$, 58002-47-4; $\text{K}_{0.60}\text{Ir}(\text{CO})_2\text{Cl}_2$, 58002-48-5; $\text{Na}_{0.93}\text{Ir}(\text{CO})_2\text{Cl}_{2.32}$, 58002-49-6; $(\text{TTF})_{0.61}\text{Ir}(\text{CO})_2\text{Cl}_2$, 58002-50-9; $\text{K}_{0.57}\text{Ir}(\text{CO})_2\text{Br}_2$, 58002-51-0; $\text{Cs}_{0.60}\text{Ir}(\text{CO})_2\text{Br}_2$, 58002-52-1; $(\text{Ph}_4\text{As})\text{Ir}(\text{CO})_2\text{Cl}_2$, 15152-88-2; $(\text{Ph}_4\text{As})_2\text{Ir}_2(\text{CO})_4\text{Cl}_6$, 58002-54-3; K_3IrCl_6 , 14024-41-0; K_2IrCl_6 , 16920-56-2.

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