TABLE II

SELECTED INFRARED FREQUENCIES ($cm^{-1}$) OF PRODUCTS FROM REACTIONS OF HYDROGEN HALIDES (HX) AND *trans*-$L_2Ir(CO)Y$ IN VARIOUS SOLVENTS (Y IS HALOGEN OR PSEUDOHALOGEN; L IS PHOSPHINE OR ARSINE)

| L | Y | HX | Solvent | Ir–H | IrC–O | Ir–Cl |
|---|---|---|---|---|---|---|
| $(C_6H_5)_3P$ | Cl | HBr | $C_6H_6$–$CH_3OH$ | 2235 | 2074 w, 2020 vs. | 307, 264 |
| $(C_6H_5)_3P$ | Cl | HBr | $C_6H_6$–$CH_3CN$ | 2239 | 2021 | 305, 264 |
| $(C_6H_5)_3P$ | Cl | HBr | $HC(O)N(CH_3)_2$ | 2227, 2235 sh | 2021 | 306, 258 |
| $(C_6H_5)_3P$ | Cl | HBr | $CHCl_3$ | 2238 | 2019 | 264 |
| $(C_6H_5)_2CH_3P$ | Cl | HBr | $C_6H_6$–$CH_3OH$ | 2216, 2204 | 2044 | 304, 265 |
| $(C_6H_5)_3As$ | Cl | HBr | $C_6H_6$–$CH_3OH$ | 2200 | 2020 | 306 vw, 263 vw |
| $(C_6H_5)_3P$ | Br | HCl | $C_6H_6$–$CH_3OH$ | 2236 | 2021 | 308, 260 |
| $(C_6H_5)_3P$ | Br | HCl | $C_6H_6$–$CH_3CN$ | 2235 | 2020 | 306, 259 |
| $(C_6H_5)_3P$ | Br | HCl | $HC(O)N(CH_3)_2$ | 2236, 2225 | 2020 | 308, 259 |
| $(C_6H_5)_3P$ | Br | HCl | $CHCl_3$ | 2226 | 2022 | 306 |
| $(C_6H_5)_2CH_3P$ | Br | HCl | $C_6H_6$–$CH_3OH$ | 2216, 2204 | 2044 | 310, 264 |
| $(C_6H_5)_3P$ | I | HCl | $C_6H_6$–$CH_3OH$ | 2235, 2203 | 2018 | 300, 256 |
| $(C_6H_5)_3P$ | Cl | HI | $C_6H_6$–$CH_3OH$ | 2210$^a$ | 2047$^a$ | 306, 260 |
| $(C_6H_5)_3P$ | Cl | HI | $C_6H_6$–$CH_3CN$ | 2218$^a$ | 2045$^a$ | 306, 258 |
| $(C_6H_5)_3P$ | Cl | HI | $HC(O)N(CH_3)_2$ | 2208$^a$ | 2047$^a$ | 305 |
| $(C_6H_5)_3P$ | Cl | HBr | $CH_2Cl_2$ | 2228 | 2021 | 305, 256 |
| $(C_6H_5)_3P$ | Br | HCl | $CH_2Cl_2$ | 2228 | 2050, 2020 | 306, 260 vvw |
| $(C_6H_5)_2CH_3P$ | Cl | HBr | $C_6H_6$–$(C_2H_5)_2O$ (wet) | 2214, 2205 | 2044 | 308, 262 |
| $(C_6H_5)_2CH_3P$ | Br | HCl | $C_6H_6$–$(C_2H_5)_2O$ (wet) | 2245, 2220 | 2030, 2020 | 308, 261 |

$^a$ In $CH_2Cl_2$ solution; all other frequencies in Nujol.

mixtures of *cis* and *trans* isomers in ionizing solvents, contrasted to the stereospecifically *cis* products obtained in benzene. Among the numerous routes by which mixtures of isomers can originate, the following most obvious pathways were briefly considered.

(1) **Isomerization during Work-up.**—Far-infrared spectra ($\nu_{Ir-Cl}$ frequencies) of products in the benzene reaction solution were virtually identical with the solid-state spectra of products obtained by either stripping the solvent or precipitation with methanol, hexane, or diethyl ether. This indicates that isomerization during work-up is not significant under mild conditions. An nmr spectrum of the solution of reactants HBr and *trans*-$[P(CH_3)(C_6H_5)_2]_2IrCOCl$ in benzene showed a triplet at $\tau$ 8.05 denoting the *trans* orientation of phosphine ligands. This spectrum is identical with that of the products obtained after precipitation with methanol. Rearrangements of phosphine ligands with variation of solvent such as was observed in the addition of allylic halides to iridium(I) complexes can thus be excluded.[7]

(2) **Substitution of Halogen in a Six-Coordinate Product.**—Treatment of a solution of 50 mg of $[CH_3(C_6H_5)_2P]_2Ir(CO)Br \cdot HBr$ with 100 mg of tetramethylammonium chloride in 5 ml of methanol gave a product which had an infrared spectrum indicating Cl incorporation in both *cis* and *trans* positions relative to the hydride. Similar treatment of $[CH_3(C_6H_5)_2P]_2Ir(CO)Br \cdot HBr$ with anhydrous hydrogen chloride in dry benzene solution resulted in no detectable substitution of Br by Cl atoms. Treatment of *trans*-$[(C_6H_5)_3P]_2Ir(CO)Cl$ with excess HBr in benzene–methanol results in a product with no $\nu_{Ir-Cl}$.

(3) **Substitution of Halogen before Addition.**—Exchange reactions of square-planar $d^8$ rhodium complexes are extremely rapid.[11] When a solution of 100 mg of *trans*-bromobis(triphenylphosphine)carbonyliridium(I) in 10 ml of benzene was treated with a solution of 100 mg of tetramethylammonium chloride in 5 ml of methanol, a yellow product with $\nu_{Ir-Cl}$ at 314 $cm^{-1}$ was obtained within 2 min.

These results indicate that the addition of anhydrous hydrogen halide (HX) to *trans*-halobis(arylphosphine)-carbonyliridium(I) complexes gives *cis* HX adducts in benzene or chloroform. In the presence of solvents such as methanol, acetonitrile, water, or dimethylformamide, which have the capacity of solvating ions, mixtures of *cis* and *trans* isomers are formed. Whether these isomers result from rapid exchange of halide ions before the addition reaction or exchange of halide ions in the products remains to be explored.

**Acknowledgment.**—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This research was also supported in part by the National Science Foundation through the GY-6152 College Science Improvement Program.

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## Reactions of Eight-Coordinate Metal Cyanide Complexes. II.[1] Interaction of Octacyanomolybdate(IV) with Uranyl Salts

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*Received November 10, 1969*

The addition of amine molecules to octacyanomolybdate(IV) results in the formation of red compounds for

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[11] H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.*, 358 (1960).

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[2] Alfred P. Sloan Foundation Fellow.

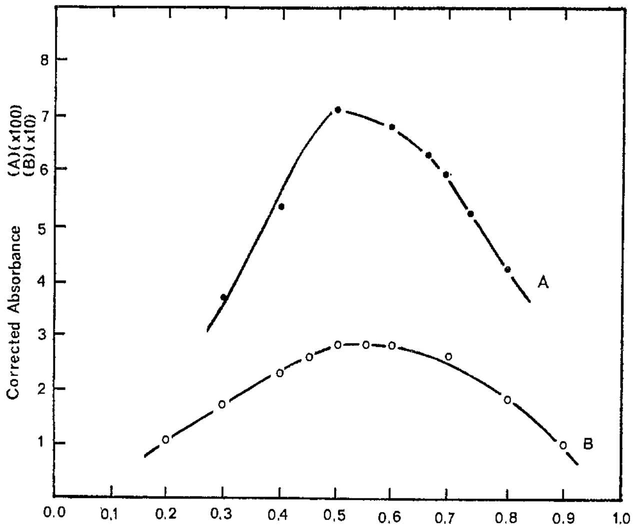

Figure 1.—Representative continuous variation plots for the reaction between uranyl and octacyanomolybdate(IV) ions in solution: curve A, λ 418 nm, total concentration of ions 1.0 × $10^{-3}$ *M;* curve B, λ 550 nm, total concentration of ions 5.0 × $10^{-3}$ *M*. *X* is the mole fraction of uranyl ion.

which decacoordinate, bicapped square-antiprismatic structures have been postulated.[3] A two-dimensional X-ray diffraction study[4] of one of these compounds, $Cd_2[Mo(CN)_8]\cdot 2N_2H_4\cdot 4H_2O$, appears to support such a structural speculation.[5] Another reaction in which the molybdenum atom of $[Mo(CN)_8]^{4-}$might expand its coordination sphere occurs when aqueous solutions of uranyl ($UO_2^{2+}$) salts are mixed with potassium octacyanomolybdate(IV). The reaction is characterized by a striking yellow to red-brown color change,[6] which could result from the interaction of oxygen atoms of the linear uranyl groups with the molybdenum atoms of $[Mo(CN)_8]^{4-}$ ions. Alternatively, the nitrogen atoms of the coordinated cyanide ligands could bind to the uranyl groups, an attractive possibility since uranyl ions are known to form brown complexes with ferrocyanide[7-9] and since aquated $Fe^{3+}$ and $Cr^{3+}$ ions produce color changes when mixed with octacyanomolybdate(IV).[10,11] In order to distinguish between these two structural alternatives and to provide further information about the uranyl–octacyanomolybdate(IV) reaction, the experiments described in the present note were carried out.

## Experimental Section

**Reagents and Physical Measurements.**—Potassium octacyanomolybdate(IV) was prepared by the method of Furman and Miller[12] from reagent grade materials. Uranyl salts were of highest purity available commercially. Chemical microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra of solid samples pressed into KBr pellets were recorded with a Perkin-Elmer Model 621 spectrophotometer. Visible and ultraviolet spectra of aqueous solutions were taken on a Cary Model 14 or Model 15 recording spectrometer using matched quartz cells of 1-cm path length.

**Hydrated Uranyl Octacyanomolybdate(IV), $(UO_2)_2Mo(CN)_8\cdot nH_2O$.**—When an aqueous solution of $K_4[Mo(CN)_8]\cdot 2H_2O$ (bright yellow) was mixed with a solution of $UO_2(NO_3)_2\cdot 6H_2O$ (pale yellow) or any other uranyl salt such as $UO_2Cl_2$ or $UO_2(C_2H_3O_2)_2\cdot 2H_2O$, there was an immediate color change to red-brown. Addition of acetone to 50 ml of an aqueous solution, 0.01 *M* in octacyanomolybdate(IV) and 0.02 *M* in uranyl ion, produced a red-brown solid. As judged by infrared spectroscopy (*vide infra*), the nature of the solid was unaffected by the particular choice of uranyl anion. The solid was filtered, washed with acetone, and dried in air; yield, 0.459 g (~95%); mp >345°. *Anal.* Calcd for $(UO_2)_2Mo(CN)_8\cdot nH_2O$: $n = 6$: C, 10.09; H, 1.27; N, 11.77; $n = 8$: C, 9.57; H, 1.61; N, 11.16; K, 0.0. Found (two separate preparations): C, 10.21, 9.75; H, 0.96, 1.25; N, 10.74, 10.71; K, 0.22.

It was also possible to prepare the compound, in very small quantities, by mixing saturated but very dilute methanol solutions of $K_4[Mo(CN)_8]\cdot 2H_2O$ with uranyl salts and collecting the solid that formed. *Anal.* Found (two separate preparations): C, 10.73, 9.74; H, 2.03, 1.17; N, 10.68, 11.07. The red-brown solids were soluble only in aqueous media. Attempts to prepare well-developed crystals from water solutions for X-ray diffraction studies were unsuccessful. Slow evaporation of a water droplet of solution produced long, thin, polymer-like ribbons of red-brown material.

## Results and Discussion

The stoichiometry of the reaction between uranyl salts and octacyanomolybdate(IV) in solution was investigated by the method of continuous variations.[13-15] This approach was possible because of the development of an intense charge-transfer[16] absorption band, the tail of which extends across the entire visible region of the spectrum. Such a band is absent in the electronic spectra[17,18] of $[Mo(CN)_8]^{4-}$ and $[UO_2(H_2O)_6]^{2+}$. Plots of the corrected change in absorbance[15] at several wavelengths against the mole fraction of added uranyl ion exhibit maxima at 0.5 for $10^{-3}$ *M* total concentration of ions (Figure 1, curve A). This behavior is indicative of 1:1 complex formation,[13-15] a result also obtained for the ferric and chromic octacyanomolybdate(IV) systems.[10,11] The plots are not exactly symmetric about the midpoint, however, which usually suggest the presence of more than one complex species in solution.[14] At 5 × $10^{-3}$ *M* total ion concentration, the maxima at various wavelengths actually shift slightly to ~0.55 (Figure 1, curve B). In view of this behavior, no attempt was made to obtain equilibrium or other thermodynamic constants for this system.

Although the spectral studies establish that a 1:1 uranyl–octacyanomolybdate(IV) complex forms in

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[3] W. Jakób, A. Samótus, and Z. Stasicka, *Roczniki Chem.*, **40**, 1383 (1966), and references contained therein.

[4] J. Chojnacki, J. Grochowski, L. Lebioda, B. Oleksyn, and K. Stadnicka, *ibid.*, **43**, 273 (1969).

[5] For further references to and discussion of this topic, *cf.* (a) J. R. Perumareddi, *Z. Naturforsch.*, **21b**, 22 (1966); (b) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

[6] This observation was first reported nearly 40 years ago,[7] but the reaction was not studied in detail at that time.

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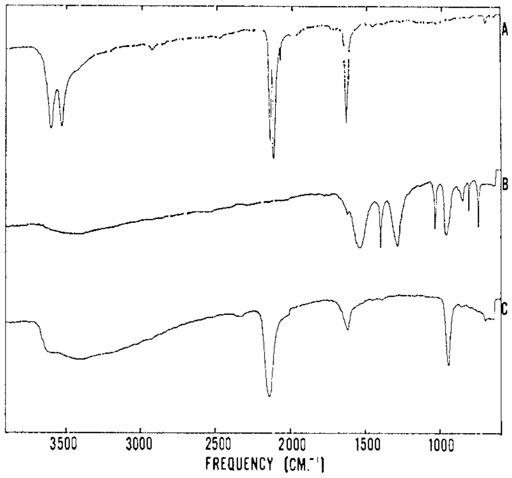

Figure 2.—Infrared spectra of (A) $K_4[Mo(CN)_8]\cdot 2H_2O$, (B) $UO_2(NO_3)_2\cdot 6H_2O$, and (C) $(UO_2)_2[Mo(CN)_8]\cdot nH_2O$ in KBr disks.

solution, the solid materials analyze as $(UO_2)_2Mo(CN)_8\cdot nH_2O$, $n \sim 6$–8. The second uranyl group in the solid is apparently required for electroneutrality. Potassium ions, present in solution, were not detected in the solids by chemical analysis. One possible structural rationalization for the stoichiometry of the solids, suggested by the solution spectral results, is represented by the formula $[UO_2(H_2O)_6]_n[UO_2(H_2O)_2Mo(CN)_8]_n$. Here the uranium atom of the cation achieves eight-coordination by bonding to six water molecules in the hexagonal plane, in the usual manner.[5b] In order to complete the hexagonal coordination belt of the uranyl group associated with the anion, the nitrogen atoms of the $[Mo(CN)_8]^{4-}$ complex might bond to the uranium atoms to form some kind of polymeric structure. Other polymeric structures in which *both* uranyl groups are bonded to the nitrogen atoms of the anion are also possible.

Evidence for the participation of the cyanide ligands in uranyl binding was obtained from infrared spectral studies of the solids. In Figure 2 are displayed the infrared spectra of $UO_2(NO_3)_2\cdot 6H_2O$, $K_4[Mo(CN)_8]\cdot 2H_2O$, and $(UO_2)_2[Mo(CN)_8]\cdot nH_2O$. From the figure it is apparent that the sharp, distinct bands in the cyanide stretching frequency region (2050–2140 $cm^{-1}$) of $[Mo(CN)_8]^{4-}$ are replaced by a broad envelope centered at 2140 $cm^{-1}$ in the red-brown adduct. This result is consistent with $Mo—C{\equiv}N—UO_2$ binding, as proposed above. It is, moreover, evident from the infrared spectra that the oxygen atoms of the linear uranyl group interact very weakly if at all with the molybdenum atoms, since the asymmetric O–U–O stretching frequency,[19] $\sim$940 $cm^{-1}$, is unaltered upon adduct formation.

Infrared spectra of the red-brown adducts formed from uranyl chloride or uranyl acetate were identical with that obtained for the uranyl nitrate (Figure 2), confirming that simple anions present in solution do not coprecipitate with octacyanomolybdate(IV). When solutions of $K_4[W(CN)_8]\cdot 2H_2O$ were added to solutions of uranyl salts, a red-brown color developed. The presumably analogous tungsten system was not studied further. Attempts to examine the photochemical behavior[1] of aqueous solutions of $(UO_2)_2[Mo(CN)_8]\cdot nH_2O$ were unsuccessful because of interference from the known photoreduction[20] of the uranyl ion.

In summary, it may be concluded from the present study that the red-brown color that appears when $[Mo(CN)_8]^{4-}$ and $UO_2^{2+}$ ions are allowed to react in aqueous solution does not correspond to an increase in the coordination number of the molybdenum atom. Instead, it has been shown that the nitrogen atoms of the cyanide ligands are bonded to the uranyl groups to form a complex which is probably polymeric.

**Acknowledgments.**—We are grateful to the National Science Foundation for financial support of this work, to a reviewer for pointing out relevant literature, and to Miss S. Hoffer for experimental assistance.

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## Nuclear Magnetic Resonance Studies of the Stereochemistry of Dichlorobis(β-diketonato) Complexes of Germanium(IV)

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*Received December 8, 1969*

All of the group IV metals with the exception of lead(IV) are known to form acetylacetonate complexes of the type $M(acac)_2Cl_2$. The constitution of $Si(acac)_2Cl_2$ in solution is uncertain,[1] but the Ti(IV),[2–4] Zr(IV),[5,6] Hf(IV),[5,6] Ge(IV),[7] and Sn(IV)[7–9] complexes are monomeric and have been assigned *cis* configurations. Neither these complexes nor their known derivatives with other β-diketonato or halo ligands have been shown to adopt a *trans*-dihalo structure.[9a]

The nmr studies reported here establish the existence of both *cis* and *trans* structures for the dichlorobis(β-diketonato)germanium(IV) complexes $Ge(dpm)_2Cl_2$ and $Ge(pvac)_2Cl_2$, where dpm = $(t\text{-}C_4H_9)COCHCO(t\text{-}C_4H_9)^-$ and pvac = $(t\text{-}C_4H_9)COCHCOCH_3^-$. Also, the nmr spectrum of $Ge(acac)_2Cl_2$ has been reinvestigated, and the results indicate that the molecule adopts a

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[9a] NOTE ADDED IN PROOF.—*cis* and *trans* octahedral configurations have been recently found for $Ti(acac)_2I_2$: R. C. Fay, Cornell University, personal communication, Dec 1969.