

TABLE II
MOLAR SOLUBILITIES OF $M(\text{acac})_2(\text{am})_2$ COMPOUNDS IN CCl_4

| Adduct | —Soly $\times 10^2$ — | | Adduct | —Soly $\times 10^2$ — | |
|--------|-----------------------|----------|--------|-----------------------|----------|
| | Ni compd ^a | Co compd | | Ni compd ^a | Co compd |
| nha | 0.75 | 1.9 | hda | Insol | <0.3 |
| noa | 0.78 | 2.2 | aa | 0.28 | 1.8 |
| nua | 1.2 | 5.8 | uena | 4.8 | 19 |
| trda | 0.67 | 1.7 | ola | 8.9 | 24 |
| ttda | <0.2 | 1.1 | lla | 9.1 | 24 |

^a Solubilities calculated from visible absorption spectra of saturated solutions.

nickel complexes. (2) The length of the amine hydrocarbon chain. The *n*-alkylamine adducts show an increase in solubility with increasing chain length, followed by a sharp decrease. Of the complexes of *n*-alkylamines prepared, the undecylamine adduct is the most soluble and the hexadecylamine adduct the least soluble. (3) Unsaturation in the amine hydrocarbon chain. The presence of double bonds in the long chains greatly increases the solubility of the adducts. The uena adducts are several times as soluble as the nua adducts, and the ola and lla adducts are still more soluble.

Recently, Rapp and Pavkovic¹⁷ reported the preparation of complexes of the type $[\text{Ni}(\text{am})_6](\text{ClO}_4)_2$, where am is a long-chained primary amine. They found that the chain length of the amine had no influence upon ease of complex formation. In this work, chain length was found to have no influence upon ease of adduct formation; of the properties measured, the only ones affected by chain length are melting point and solubility.

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Preparation and Coordination Chemistry of 1,4-Cyclooctadiene

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Very little attention has been paid to the reactions of 1,4-cyclooctadiene (1,4-COD) with transition metal ions, in comparison with the extensively investigated 1,5-COD and 1,3-COD.¹ This is due to the fact that the known methods of preparation of 1,4-COD are either tedious² or involve rather expensive starting materials.³

1,4-COD has been encountered as a reaction intermediate in the homogeneous catalytic isomerization of

1,5-COD to 1,3-COD⁴ and in the rearrangement of coordinated 1,3-COD to 1,5-COD in Pd(II) complexes.⁵ Information on the coordination chemistry of 1,4-COD may, therefore, throw some light on the mechanisms of these isomerization and rearrangement reactions.

The present work has been undertaken to find a convenient method for the preparation of 1,4-COD, and to investigate reactions of 1,4-COD with some transition metal ions.

Experimental Section

Materials.—*cis*-Pt $\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2$ ^{6,7} and Pd $(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ ⁸ were prepared by methods reported in the literature. 1,5-COD were distilled under reduced pressure before use. Its purity was checked by gas chromatography.

1,4-COD was prepared by the controlled isomerization of 1,5-COD. Two grams of Pt $\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2$ and 5.0 g of SnCl₂·2H₂O were dissolved in 150 ml of CH₂Cl₂. 1,5-COD (300 ml) was added and the reaction mixture was stirred in a Parr high-pressure reactor under 600 psi of hydrogen at 75° for 4 hr. The recovered COD mixture (275 ml) consisted of 36% 1,5-COD, 42% 1,4-COD, and 22% 1,3-COD. 1,5-COD was separated from the diene mixture by an efficient fractionating column. 1,4-COD was separated from the mixture of 1,3-COD and 1,4-COD by the method of AgNO₃ adduct formation.⁹ Seventy-five milliliters of pure (>99.5% by VPC) 1,4-COD was obtained; bp 114.2° (758 mm); *n*²⁰_D 1.4894; ir (neat): 1645 (C=C); nmr (CCl₄) consisted of four multiplets due to 4, 2, 4, and 2 H's, respectively, centered at τ values of 4.48 (-(H)C=C(H)-), 7.23 (=CC(H₂)-C=), 7.72 (=CC(H₂)-C-), and 8.60 ppm (=CCC(H₂)CC=).

Reactions of 1,4-COD with Some Transition Metal Ions.—Some of the properties of the products of the reaction of 1,4-COD with some transition metal ions are shown in Table I.

RhCl₃·3H₂O.—To a solution of 0.50 g of RhCl₃·3H₂O in 10 ml of absolute ethanol 1 ml of 1,4-COD was added and the mixture was stirred for 2.5 hr at 60°. A complex identical with [Rh(1,5-COD)Cl]₂⁹ was obtained.

Attempts to prepare a complex of Rh(I) in which 1,4-COD is unrearranged, by running the reaction at 3–4° for 2 days, have failed.

IrCl₃·3H₂O.—The reaction was carried out in a manner similar to that of RhCl₃·3H₂O for 12 hr. A complex identical with [Ir(1,5-COD)HCl]₂¹⁰ was obtained.

Pd(C₆H₅CN)₂Cl₂.—To a solution of 0.50 g of Pd(C₆H₅CN)₂Cl₂ in 10 ml of benzene was added 1 ml of 1,4-COD. The yellow precipitate obtained was filtered and washed with benzene and petroleum ether (bp 30–75°), respectively. *Anal.* Calcd for C₈H₁₂Cl₂Pd: C, 33.81; H, 4.25; Cl, 24.61. Found: C, 33.90; H, 4.32; Cl, 24.48.

When a suspension of 1.00 g of Pd(C₆H₅CN)₂Cl₂ in several milliliters of 1,4-COD was stirred for 1.5 hr, a yellow precipitate separated; mp 185–198 dec. Decomposition of the product with aqueous KCN gave a mixture of 1,4-COD and 1,5-COD.

K₂PtCl₄.—A solution of 0.50 g of K₂PtCl₄ in 30 ml of 50% ethanol containing 1 ml of 1,4-COD was stirred overnight. The white compound obtained was recrystallized from acetic acid. Although analysis for the olefin shows it to be Pt(1,5-COD)Cl₂, the complex is different from that obtained by the reaction of K₂PtCl₄ with 1,5-COD under similar conditions.

CuCl.—The reaction of 1,4-COD with CuCl in aqueous HCl or with CuCl₂·2H₂O in ethanol in the presence of a reducing agent gave [Cu(1,4-COD)Cl]₂. *Anal.* Calcd for C₈H₁₂ClCu: Cu, 30.7. Found: Cu, 30.2.

AgNO₃.—Reaction of 1 ml of 1,4-COD with 3 ml of 50% aqueous AgNO₃ solution gave [Ag₂(1,4-COD)](NO₃)₂. *Anal.* Calcd for C₈H₁₂N₂O₆Ag₂: Ag, 48.2. Found: Ag, 48.3. Equivalent conductance of a 0.01 M aqueous solution is 5.1 ohm⁻¹ cm² corresponding to a 1:2 electrolyte.

HAuCl₄.—An unstable, light-sensitive compound was obtained

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TABLE I
 REACTIONS OF 1,4-COD WITH SOME TRANSITION METAL IONS

| Reactant | Product | Color | Mp (dec), °C | —Ir— | Olefin obtained upon decompn ^a |
|---|--|--------|-----------------|---|--|
| RhCl ₃ ·3H ₂ O | [Rh(1,5-COD)Cl] ₂ | Yellow | 220 | | 1,5-COD |
| IrCl ₃ ·3H ₂ O | [Ir(1,5-COD)HCl ₂] ₂ | Yellow | 198 | $\nu_{\text{Ir-H}}$, 2256 | 1,5-COD |
| Pd(C ₆ H ₅ CN) ₂ Cl ₂ | Pd(1,4-COD)Cl ₂ | Yellow | 141 | $\nu_{\text{C=C}}$, 1510 | 1,4-COD |
| K ₂ PtCl ₄ | Pt(1,5-COD)Cl ₂ | White | 138–139 | | 1,5-COD |
| CuCl | [Cu(1,4-COD)Cl] ₂ | White | 113–114 | $\nu_{\text{C=C}}$, 1615, 1495 $\nu_{\text{Cu-Cl}}$ (bridging), 348, 320 | 1,4-COD |
| AgNO ₃ | [Ag(1,4-COD)Ag](NO ₃) ₂ | White | 110–111 | $\nu_{\text{C=C}}$, 1600 | 1,4-COD |
| HAuCl ₄ | Unstable | White | | | 1,4-COD |

^a Decomposition was accomplished by treating the complex with aqueous KCN and extracting the olefin with ether. The AgNO₃ complex was decomposed with aqueous NH₃ solution.

by the reaction of 0.50 g of HAuCl₄ in 20 ml of H₂O with 1 ml of 1,4-COD.

Results and Discussion

1,4-COD can be conveniently prepared by optimizing the conditions of the homogeneous catalytic isomerization of 1,5-COD to 1,3-COD to give a maximum yield of the intermediate 1,4-COD. The number of moles of 1,5-COD used per mole of the catalyst is 1000. The catalyst can be recovered and reused frequently with no decrease in its catalytic activity. However, small amounts of SnCl₂·2H₂O must be added every time a second-hand catalyst is used.

1,4-COD reacts readily with transition metals with almost-filled d orbitals in their low oxidation states. This reflects the importance of π bonding involving electron back-donation in the olefin-metal complexes. The behavior of Ir(III) which, unlike Rh(III), retains its high oxidation state may suggest that π bonding in Ir, and probably in other heavier atoms, is less important than σ bonding.

Ions which are known to react with 1,3-COD react readily with 1,4-COD. Thus Ag(I) which gives a complex with 1,5-COD stable in solution up to 75° and a complex with 1,3-COD stable in solution only below 0° gave a 1,4-COD-Ag^I complex stable at 40° in solution. The behavior of 1,4-COD with Pd(II) *vs.* that of 1,3-COD and 1,5-COD parallels its behavior with Ag(I). Moreover, some ions, *e.g.*, Cu(I), which do not react with 1,3-COD but give stable complexes with 1,5-COD, did give rather unstable complexes with 1,4-COD. This intermediate behavior of 1,4-COD may be attributed to the position of the two double bonds in the olefin. They are far enough from each other to give complexes more stable than those of 1,3-COD and too close to give complexes as stable as those of 1,5-COD.

Closer examination of the behavior of Ag(I) shows this steric effect very clearly. 1,5-COD may span the two coordination sites on opposite sides of the Ag⁺ ion, though not necessarily at exactly 180°, thus forming [Ag(1,5-COD)]⁺NO₃⁻. 1,4-COD, on the other hand, acts as a bridge between two Ag⁺ ions giving [Ag(1,4-COD)Ag]²⁺(NO₃)₂²⁻.

The ir spectrum of the 1,4-COD-Cu^I complex shows two absorptions assigned to C=C at 1615 and 1495 cm⁻¹. This suggests that one double bond is much closer to the metal atom than the other. It also reflects the weaker bonding in [Cu(1,4-COD)Cl]₂ compared to that in [Cu(1,5-COD)Cl]₂ in which $\nu_{\text{C=C}}$ is reduced by about 165 cm⁻¹ from its free-olefin value.

The transition metal ions investigated in this work can be classified into three categories with respect to

their reaction with 1,4-COD. (1) Ions which give 1,4-COD-metal complexes. The olefin does not rearrange in these complexes. These ions include Ag(I), Cu(I), and Au(III). (2) Ions which give 1,5-COD-metal complexes. 1,4-COD rearranges in complexes of these ions to the better chelating 1,5-COD. Such ions include Pt(II), Rh(III), and Ir(III). These same ions are known to yield 1,5-COD-metal complexes in their reaction with 1,3-COD. The rearrangement of 1,3-COD to 1,5-COD in these complexes probably proceeds *via* the intermediate formation of 1,4-COD which rearranges in a very fast step to the 1,5 isomer.⁶ This explains the failure to detect 1,4-COD as reaction intermediate in the 1,3 to 1,5 rearrangement by these ions. (3) Ions which may give 1,4-COD-metal complex or rearranged 1,5-COD-metal complex depending on the reaction conditions. Pd(II) stands unique in this category. The reason for the different behaviors of various ions may be related to the size of the ion involved.

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Kinetic Differences between the Incorporation of Zinc(II) and Cadmium(II) into Porphyrins and N-Methylporphyrins¹

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While a number of studies have appeared concerning the mechanisms of incorporation of divalent metal ions into porphyrin molecules to form metalloporphyrins,^{2–13}

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