

fluoride solution) containing 7.93 g. of AgF was added. After removal of the silver bromide the filtrate was evaporated to dryness and the product recrystallized from alcohol. The yield was 2.62 g., 42%.

Trimethylantimony dinitrate and trimethylantimony sulfate were prepared from trimethylantimony dibromide and silver nitrate or silver sulfate in aqueous solution by the same procedure as used for the difluoride.

Trimethylantimony Dihydroxide.—Although this compound has been prepared from moist silver oxide and trimethylantimony dihalides, solutions of trimethylantimony dihydroxide dissolve considerable amounts of silver ion, and it is difficult to prepare pure trimethylantimony dihydroxide by this procedure. We have found that when a hot aqueous solution of trimethylantimony dichloride (9.5 g. in 1 l. of water) was passed through a column of Amberlite IR4B and the resulting aqueous solution evaporated to dryness by means of a Rinco evaporator, trimethylantimony dihydroxide was obtained as a sirup which crystallized on scratching with a stirring rod. The compound was readily recrystallized from acetone; the yield was 85%. Trimethylantimony dihydroxide on heating *in vacuo* at 110° loses 1 mole of water to give the hygroscopic trimethylantimony oxide.

Oxybis-(trimethylantimony) Diperchlorate.—A solution of 3.26 g. of trimethylantimony dibromide in 165 ml. of hot water was mixed with a solution of 4.14 g. of silver perchlorate in 30 ml. of water. After removal of the silver bromide the filtrate was diluted to 200 ml. in a volumetric flask. Aliquots of this solution (20 ml.) were evaporated in desiccators over calcium chloride. After several days, white crystals and a sirupy liquid (probably perchloric acid) were obtained. In several cases explosions occurred during the final stages of the evaporation procedure, and preparation on a larger scale is extremely hazardous. The white crystals were very carefully removed by means of a rubber policeman, dried on a porous plate, washed with anhydrous ether, and dried over calcium chloride *in vacuo*. The resulting crystals proved to be quite insensitive to mechanical shock and decomposed on heating without exploding. Analysis of the compound corresponded to the formula $(\text{Me}_3\text{SbClO}_4)_2\text{O}$. The same analysis was obtained when the crystals were air dried; *i.e.*, there was no evidence that $\text{Me}_3\text{Sb}(\text{OH})\text{ClO}_4$ separated from solution. We also performed the experiment with solutions of trimethylantimony dibromide and silver perchlorate in absolute alcohol. Again we obtained only $(\text{Me}_3\text{SbClO}_4)_2\text{O}$, and again there were several cases in which explosions occurred during the evaporation procedure.

Oxybis-(trimethylantimony) dichloride was prepared by mixing aqueous solutions of trimethylantimony dichloride (1.1883 g.) and trimethylantimony dihydroxide (1.0037 g.) and evaporating the resulting solution to a small volume. The white crystals which

separated from solution were recrystallized from alcohol. The yield was 1.55 g., 71%.

Triethylantimony dibromide was originally reported by Löwig and Schweizer, who reported that the compound could not be distilled.¹⁹ More recently Hartmann and Kühl reported that triethylantimony dibromide can be purified by distillation; b.p. 107° (90 mm.).¹⁰ They do not report analyses on the distilled compound. We have been unable to distill triethylantimony dibromide even at 0.2 mm. without decomposition. Accordingly, we purified the dibromide (m.p. -10°) by recrystallization from alcohol at low temperatures and filtration through a cold funnel. We were unable, however, to obtain an analytically pure sample; the compound always contained slightly more than the theoretical antimony.

Triethylantimony sulfate was prepared from the dibromide and silver sulfate in 70% alcohol. It was recrystallized from alcohol; the yield was 45%.

Trimethylstibine was prepared from trimethylantimony dibromide and granulated zinc by the method of Morgan and Yarsley.⁷ For the purpose of obtaining infrared spectra, the stibine was distilled into ampoules containing the necessary solvent (CS_2 or CCl_4) and the ampoules sealed at the conclusion of the distillation. The ampoules were opened and appropriate dilutions made in a drybox in a nitrogen atmosphere.

The Reaction between Trimethylantimony Dihydroxide and Hydrochloric Acid.—Trimethylantimony dihydroxide (1.6 g.) was dissolved in 10 ml. of water and 10 ml. of concentrated hydrochloric acid added. The dense white precipitate was removed by filtration, dried, and recrystallized from alcohol. The compound gave analytical values and an infrared spectrum identical with trimethylantimony dichloride. The recovery was 80%.

The Hydrolysis of Trimethylantimony Cyanobromide.—Trimethylstibine, prepared by reduction of the dibromide with zinc dust in a nitrogen atmosphere, was distilled into a solution of cyanogen bromide in petroleum ether. The precipitate was removed by filtration and dissolved in warm water. The clear solution was evaporated to a small volume, and the crystals that resulted were recrystallized twice from alcohol. The analysis and infrared spectrum of these were identical with the analysis and spectrum of trimethylantimony dibromide.

Acknowledgments.—The authors wish to acknowledge the skilled technical assistance of Miss Mary Elizabeth Key. The infrared spectra below 550 cm.^{-1} were performed by the Perkin-Elmer Corp., Norwalk, Conn., whose help is gratefully acknowledged.

(19) C. Löwig and E. Schweizer, *Ann.*, **75**, 315 (1850).

[CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Reactions of Coordinated Ligands. VI. Metal Ion Control in the Synthesis of Planar Nickel(II) Complexes of α -Diketo-bis-mercaptoimines

BY MAJOR C. THOMPSON AND DARYLE H. BUSCH

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A series of nickel(II) complexes has been synthesized with the tetradentate Schiff base ligands formed between α -diketones and β -mercaptoethylamine. Although the formation of the α -diimine is strongly discriminated against under ordinary conditions, the reaction of the ligand components in the presence of nickel(II) ion results in high yields of the desired complexes. The α -diketones used were: biacetyl, 1,2-cyclohexanedione, 2,3-octanedione, 2,3-pentanedione, and 1-phenyl-1,2-propanedione. The planar complexes have been characterized by elemental analysis and through the determination of molecular weights, infrared spectra, solubilities, and magnetic moments. Two classes of template reaction have been defined.

Introduction

Several investigators have worked with bidentate and tridentate ligands containing the amine group and the mercaptide group and found that these ligands form very stable chelate compounds.¹⁻⁷ It has been shown that mercaptoamines will produce diamagnetic square-planar structures with nickel(II).

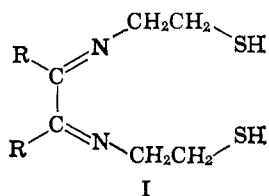
In addition to intrinsic donor ability, it is to be an-

anticipated that the stereochemical relationship of the ligand to the metal ion⁵ will be of principal significance in determining the stability and nature of the metal complexes. The only tetradentate ligand containing nitrogen and mercapto donors, $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$, which has previously been prepared,⁷ is incapable of occupying all four donor positions in a square-planar coordination sphere. Most of the remaining investigations involving tetradentate ligands, both planar and nonplanar, have concerned molecules containing nitrogen and oxygen as the relatively weak donors.

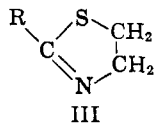
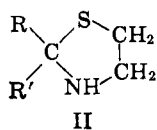
This study is concerned with a class of ligands specifically designed to provide square-planar, tetradentate coordination through nitrogen and mercapto donors.

- (1) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 265 (1936).
- (2) R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949).
- (3) R. G. Charles and H. Freiser, *J. Am. Chem. Soc.*, **74**, 1385 (1952).
- (4) S. E. Livingstone, *J. Chem. Soc.*, 1042 (1956).
- (5) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872, 878, 884 (1962).
- (6) C. A. Root, Thesis, The Ohio State University, 1962.
- (7) J. Harley-Mason, *J. Chem. Soc.*, 320 (1947).

At the initiation of these studies it was proposed that the Schiff base adducts of α -diketones with β -mercaptoalkylamines (structure I) should be ideally suited to the mode of coordination of immediate concern.



The amino groups in 2-aminothioethers readily form Schiff bases with ketones.^{8,9} Difficulty arises, however, in the synthesis of Schiff base compounds from β -mercaptoanines and ketones. The amine and mercapto groups (in 1,2-positions) behave as competitive nucleophiles, usually resulting in the formation of thiazolines (structure II) and thiazoles (structure III).¹⁰⁻¹⁴ In some cases mercaptals are also ob-



tained.^{13,15} Barnett¹⁶ reported that the reaction of pentalactone with β -mercaptoethylamine produces a Schiff base of the desired type. The presence of free mercaptan was demonstrated by titration with iodine. In addition to studies on the reaction with aldehydes and monoketones, Elderfield and McClenachan¹⁴ carried out the reaction of benzil with *o*-aminobenzene-thiol and obtained 2,2'-biphenyl-2,2'-bibenzothiazoline. Thus it is possible to obtain three products from the reaction of β -mercaptoethylamine with an α -diketone; namely, a thiazoline, a mercaptal, or the previously mentioned Schiff base.

The present investigation reveals that the yield of the Schiff base may be enhanced to greater than 70% by the simple device of conducting the condensation in the presence of nickel(II) ion. The discussion to follow describes the synthesis of five examples of the subject class of complexes and their characterization by means of physical measurements. These substances exhibit a number of novel and interesting properties.

Experimental

Materials.— β -Mercaptoethylamine hydrochloride was obtained from Evans Chemetics, Inc., Waterloo, N. Y. 2,3-Butanedione and 2,3-pentanedione were obtained from Matheson Coleman and Bell. 2,3-Octanedione and 1-phenyl-1,2-propanedione were obtained from Eastman Organic Chemicals. 1,2-Cyclohexanedione was obtained from K and K Laboratories, Inc., New York, N. Y. All other chemicals were of reagent grade.

Magnetic Measurements.—Magnetic moments were obtained by the Gouy method using iron(II) ammonium sulfate 6-hydrate and mercury(II) tetrathiocyanatocobaltate(II) as standards. Magnetic susceptibilities listed in Table I refer to the entire compound.

Molecular Weights.—Molecular weights were measured at 37.00° in chloroform using a Mechrolab vapor pressure osmometer (Mechrolab Inc., Mountain View, Calif.). Molecular weights are reported in Table I.

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(9) T. Zincke and P. Jorg, *Ber.*, **43**, 3443 (1910).

(10) M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **47**, 3078 (1925).

(11) H. P. Lankelma and P. X. Sharnoff, *ibid.*, **54**, 379 (1932).

(12) S. Ratner and H. T. Clarke, *ibid.*, **59**, 200 (1937).

(13) F. J. Kreipa, V. Mature, J. J. Finn, J. G. McClarnon, and F. Lombardo, *ibid.*, **73**, 1155 (1951).

(14) R. C. Elderfield and E. C. McClenachan, *ibid.*, **82**, 1982 (1960).

(15) S. V. Tsukerman, *Ukrain. Khim. Zh.*, **19**, 523 (1953); *cf. Chem. Abstr.*, **49**, 8255c (1955).

(16) J. W. Barnett, *J. Chem. Soc.*, 5 (1944).

TABLE I

MOLECULAR WEIGHTS AND MAGNETIC MOMENTS OF COMPLEXES OF α -DIKETO-BIS-MERCAPTOETHYLIMINES^a

Compound	—Molecular weight—		χ_m (complex) $\times 10^6$	T, °K.
	Calcd.	Found		
Ni(BE)	261	257	-113.7	306
Ni(CE)	287	297	-55.3	297
Ni(OE)	317	298	-170.7	298
Ni(PE)	275	266	-99.4	301
Ni(PPE)	323	315	-109.1	297

^a Abbreviations used are: BE = biacetyl-bis-(mercaptoethylimine), CE = 1,2-cyclohexanedione-bis-(mercaptoethylimine), OE = 2,3-octanedione-bis-(mercaptoethylimine), PE = 2,3-pentanedione-bis-(mercaptoethylimine), PPE = 1-phenyl-1,2-propanedione-bis-(mercaptoethylimine).

Infrared Spectra.—The spectra of the complexes (Table II) were obtained by KBr pellet method with a Perkin-Elmer Model 21 spectrophotometer. Calibrations were made with a polystyrene spectrum as a standard.

TABLE II

INFRARED SPECTRA OF THE NICKEL(II) COMPLEXES

Ni(BE) ^a	Ni(PE) ^b	Ni(OE) ^c	Ni(PPE) ^d
2958 m	2946 m	2957 vs	2954 m
2867 sh	2855 sh	2876 s	2862 sh
.....	1704 vw
.....	1626 wb	1622 vw
.....	1601 vw
.....	1569 vwb
1537 wb	1530 w	1527 w	1526 w
.....	1512 sh
1454 sh	1474 sh
1442 s	1456 sh	1464 m	1447 s
.....	1439 s	1435 sh
1424 m	1428 sh	1422 m
1416 m	1415 w
.....	1385
1372 s	1372 s	1372 s	1373 w
.....	1350 s	1352 s	1343 s
.....	1332 sh	1320 sh
1323 s	1326 s	1322 m	1311 vs
.....	1299 vwb	1296 vw
1276 m	1275 m	1286 w	1275 m
.....	1237 vwb	1240 s
1216 m	1207 vwb
1199 s	1192 s	1197 sh	1201 w
.....	1171 m	1174 w
1162 m	1159 w	1160 wb	1157 w
1081 wb	1097 vw	1108 w	1100 w
.....	1067 m	1039 wb	1067 w
.....	1024 m	1020 vwbsh	1016 m
997 mb	967 wb	966 m
949 w	931 wb	922 vw
.....	858 vwb	851 vwb
797 vwb	795 vwb	812 wb
.....	761 vwb	777 s
.....	722 w	749 wb
.....	667 vwb	705 vw

b = broad, m = medium, sh = shoulder, s = strong, vs = very strong, w = weak, vw = very weak. ^a BE = biacetyl-bis-(mercaptoethylimine). ^b PE = 2,3-pentanedione-bis-(mercaptoethylimine). ^c OE = 2,3-octanedione-bis-(mercaptoethylimine). ^d PPE = 1-phenyl-1,2-propanedione-bis-(mercaptoethylimine).

Analyses.—Nitrogen analyses were obtained using a Coleman Model 29 nitrogen analyzer. All other analyses were performed by Galbraith Microanalytical Laboratories.

Syntheses. **Biacetyl-bis-(mercaptoethylimine)-nickel(II).**— β -Mercaptoethylamine hydrochloride (2.27 g., 0.02 mole, approximately 10% excess) was added to a solution prepared by adding 0.42 g. (0.018 g.-atom) of sodium to 50 ml. of absolute ethanol and filtering to remove the sodium chloride that was formed. To this solution was added 0.86 g. (0.01 mole) of biacetyl, and the solution was stirred and heated for 10 min. Then, 2.47 g. (0.01 mole) of nickel(II) acetate 4-hydrate, dissolved in 25 ml.

of absolute ethanol, was added and the mixture was heated and stirred until the solution developed a dark red color and no solid remained. The solution was cooled overnight. The dark green needle-like crystals were filtered and the solution was concentrated to produce more solid. The products were then combined, dissolved in 200 ml. of boiling methanol, and filtered to remove any insoluble materials. The solution was concentrated by rotary evaporation to approximately 50 ml. and placed in the freezer overnight. The crystals were filtered and dried *in vacuo* over P_2O_5 .

The recrystallized product was composed of dark green needles, which were red to transmitted light and formed a dark red powder upon grinding. It is appreciably soluble in a variety of solvents, the colors of the solutions varying from solvent to solvent; yield 70.4%.

Anal. Calcd. for $Ni(C_8H_{14}N_2S_2)$: C, 36.81; H, 5.41; N, 10.73; S, 24.57. Found: C, 36.74; H, 5.53; N, 10.72; S, 24.37.

2,3-Pentanedione-bis-(mercaptoethylimino)-nickel (II).—

This preparation was exactly analogous to the previous one except that 1.00 g. (0.01 mole) of 1,2-pentanedione was introduced instead of biacetyl.

The recrystallized product was composed of dark green crystals which were red-brown to transmitted light and turned dark red on grinding. It is appreciably soluble in the same solvents as the previous product; yield 74.5%.

Anal. Calcd. for $Ni(C_5H_8N_2S_2)$: C, 39.30; H, 5.86; N, 10.19; S, 23.31. Found: C, 39.34; H, 5.84; N, 10.18; S, 23.19.

2,3-Octanedione-bis-(mercaptoethylimino)-nickel(II).—

This preparation was exactly analogous to the previous ones except for the addition of 1.42 g. (0.01 mole) of 2,3-octanedione.

The recrystallized product was composed of dark green crystals which were red-brown to transmitted light and turned purple-red on grinding. It is soluble in the same solvents as the previous products; yield 78.1%.

Anal. Calcd. for $Ni(C_{12}H_{22}N_2S_2)$: C, 45.44; H, 6.99; N, 8.84; S, 20.22. Found: C, 45.31; H, 6.92; N, 8.68; S, 20.02.

1-Phenyl-1,2-Propanedione-bis-(mercaptoethylimino)-nickel

(II).—This preparation was similar to the previous ones. The diketone added was 1-phenyl-1,2-propanedione. In order to obtain a solid product from the solution it was necessary to concentrate the solution to 25 ml. and place it in the freezer overnight. The same method of recrystallization was followed except the final volume was only 25–30 ml.

The final product is a dark red powder, which does not change in appearance upon grinding. Its solubility in several solvents is similar to that of the previously described compounds. The yield after recrystallization was 19%.

Anal. Calcd. for $Ni(C_{13}H_{16}N_2S_2)$: C, 48.32; H, 4.99; N, 8.67; S, 19.85. Found: C, 49.06, 47.88; H, 5.00, 4.96; N, 8.15, 8.35, 8.19; S, 19.30, 19.83.

1,2-Cyclohexanedione-bis-(mercaptoethylimino)-nickel(II).—

This preparation was exactly analogous to the previous ones except for the addition of 1.12 g. (0.01 mole) of 1,2-cyclohexanedione.

The recrystallized product was composed of dark green crystals which were red-brown to transmitted light and turned dark red on grinding. It is soluble in the same solvents as the previous products; yield, 77.0%.

Anal. Calcd. for $Ni(C_{10}H_{16}N_2S_2)$: C, 41.84; H, 5.62; N, 9.76; S, 22.34. Found: C, 41.74; H, 5.83; N, 9.74; S, 21.99.

Results and Discussion

The following new compounds have been prepared: biacetyl-bis-(mercaptoethylimine)-nickel(II), 1,2-cyclohexanedione-bis-(mercaptoethylimine)-nickel(II), 2,3-octanedione-bis-(mercaptoethylimine)-nickel(II), 2,3-pentanedione-bis-(mercaptoethylimine)-nickel(II), and 1-phenyl-1,2-propanedione-bis-(mercaptoethylimine)-nickel(II). The complexes shall be abbreviated as Ni(BE), Ni(CE), Ni(OE), Ni(PE), and Ni(PPE), respectively.¹⁷

The ligand components, β -mercaptoethylamine and α -diketone, were mixed and allowed to react for a short time. Then, nickel ion, in the form of the acetate salt, was added so that complexation might occur with the Schiff base as the latter was formed. Nickel acetate

was used rather than other salts, so that the basicity of the solution would be favorable for the formation of the metal-sulfur bond through loss of a slightly acidic hydrogen.

Attempts were made to form the desired Schiff base ligands (structure I) by the reaction of β -mercaptoethylamine and the proper α -diketone under a variety of reaction conditions and isolation procedures including those exactly the same as described in the preparations of the complexes. In each case, the main product was found to be the thiazolidine (60–75%) as shown by infrared spectra, with small yields (~10%) of the desired impure Schiff base which tended to rearrange upon attempted purification. However, this crude product combined with nickel salts forming the Schiff base complex. Other work involving β -mercaptoethylamine and cysteine condensed with ketones and aldehydes has yielded only thiazolidines.^{18–20} However, these thiazolidines were shown to give tests indicative of the presence of the free mercapto group leading to the proposal that an equilibrium is established between the thiazolidine and the Schiff base.^{19,20}

Among the more reasonable assumptions that can be made concerning the sequential aspects of the mechanism of thiazolidine formation in these systems is the supposition that the initial reaction involves formation of the Schiff base, followed by cyclization. The fact that the more stable and abundant products in the reaction of β -mercaptoamines and ketones are the thiazolidines and mercaptals suggests that the Schiff base may be regarded as an intermediate in thiazolidine formation.

On the basis of these considerations, two possible courses of reaction might be delineated to facilitate the formation of the complexes of the Schiff base despite the discrimination against this product in the organic system. One might add the metal ion during the course of the condensation process with the view that the metal ion should chelate with the intermediate, the Schiff base, and simultaneously produce the desired material and prevent the formation of thiazolidines. The design of the syntheses reported here has followed this rationale.

Alternatively, since it has been demonstrated that the thiazolidine and the Schiff base are in equilibrium,^{19,20} the direct reaction of a metal salt in basic or buffered solution would be expected to yield the Schiff base complex. In related work employing the reaction of *o*-aminophenol with α -diketones, Bayer and Schenck²¹ have shown that base as well as metal ions brings about the formation of a Schiff base from the previously formed 2,2'-bis-benzooxazolonyl compounds.²¹ Recent work has shown that when thiazolidines and benzothiazolines are heated with certain metal salts, complexes with the Schiff base ligands analogous to those in structure I²² are produced in their corresponding metal complexes. These thiazolines do not rearrange to Schiff bases in the presence of 0.1 M NaOH at room temperature.²²

In general, the addition of a metal ion will either stabilize or destabilize ligands of this class.²³ The latter situation is illustrated in the work of Eichhorn and Bailar²⁴ and Eichhorn and Trachtenberg,²⁵ who

(18) T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **27**, 2452 (1962).

(19) G. Hesse and G. Ludwig, *Ann.*, **632**, 158 (1960).

(20) M. P. Schubert, *J. Biol. Chem.*, **114**, 341 (1936).

(21) E. Bayer and G. Schenck, *Ber.*, **93**, 1184 (1960).

(22) H. Jamadus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, in press (private communication).

(23) D. H. Busch, *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p. 7.

(24) G. L. Eichhorn and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 2905 (1953).

(25) G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 5183 (1954).

(17) The International Union names for these compounds are, respectively: 2,2'-dimethyl-(ethanediylienedinitrilo)-diethanethiolonickel(II), 2,2'-(1,2-cyclohexanediylienedinitrilo)-diethanethiolonickel(II), 2-methyl-2-ethyl-(ethanediylienedinitrilo)-diethanethiolonickel(II), and 2-methyl-2'-phenyl-(ethanediylienedinitrilo)-diethanethiolonickel(II).

have shown that metal ions promote the hydrolysis of bis-(2-thiophenyl)-ethylenediimine resulting in the formation of the ethylenediimine complex of the metal and 2-thiophenylaldehyde. The first-mentioned situation may be exemplified by the works of Krumholz²⁶ and Figgins and Busch,²⁷ who found that monomeric biacetyl-bis-methylimine could only be prepared in the presence of metal ion. In the absence of an appropriate metal ion, polymeric oils were obtained. Similarly, Eichhorn and Marchand²⁸ have shown that the stability of the carbon-nitrogen double bond is increased by complexation with metal ions in the case of salicylaldehyde.

Using the preparation described here the desired complexes were usually produced in greater than 70% yield. The initial formation of small amounts of bis-(aminoethanethiolo)-nickel(II) is observed upon the addition of nickel(II) ion to solutions of biacetyl and β -mercaptoethylamine; however, this product must react with the α -diketone since it is not present at the end of the reaction. In the case of *o*-aminobenzethiol, the formation of the very insoluble bis-(amino-benzenethiolo)-nickel(II) apparently prevents formation of the tetradentate Schiff base with biacetyl.

The color and crystalline habit of the solid complexes Ni(BE), Ni(PE), Ni(OE), and Ni(CE) indicates that they are of the same family of compounds. Each forms dark green, needle-like crystals when allowed to separate from solution slowly. The crystals transmit red-brown light, however, and, upon grinding, a red-brown powder is obtained. The complex Ni(PPE) has only been obtained as a dark red-brown powder.

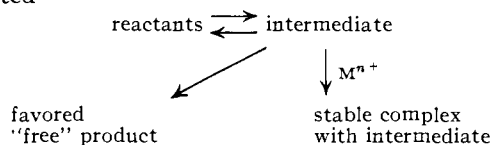
The complexes have been identified and characterized by analysis, infrared spectra, molecular weights, magnetic moments, and solubilities. Electronic spectra will be discussed in a later report. Four-element analyses have established the compositions required by the formulation. The nature of the ligand has been inferred from the infrared spectra (Table II). The absence of N-H stretching frequencies and carbonyl bands and the presence of a weak absorption at approximately 1530 cm^{-1} , corresponding to a complexed, conjugated C=N stretching mode, provide evidence for the formation of the expected Schiff base.

The compounds exhibit substantial solubilities in a wide variety of solvents ranging from water to carbon disulfide. This is in sharp contrast to the behavior of such thiazoline complexes as (2,2'-dimethyl-2,2'-bibenzothiazoline)-nickel(II) which is soluble only in pyridine.²⁹ Although discussion is reserved for a more detailed report, it is worth pointing out at this point that the colors of these compounds are strongly solvent dependent.

The molecular weight determination (Table I) clearly shows the monomeric nature of these substances, while their diamagnetism establishes the presence of the square-planar nickel(II) ion in each case (Table I).

From the manner of synthesis and the physical properties of the complexes of immediate interest it may be concluded that the metal ion mediates the condensation reaction between the α -diketone and β -mercaptoethylamine. The principal effect of the nickel(II) ion is to produce that possible reaction product which is best suited to form a stable complex. The exact manner in which such an effect occurs is of considerable significance. In this regard a number of behaviors are worthy of consideration. A purely thermodynamic

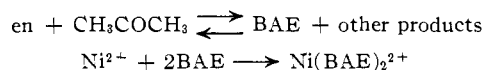
effect is to be expected in those instances in which the metal ion serves to coordinate with and thereby remove one component from an equilibrium. This is well illustrated by the previously cited observations of Eichhorn and Marchand²⁸ on the reaction of glycine and salicylaldehyde in the presence of metal ions. Such an effect will be termed an *equilibrium displacement*. At the other extreme, a metal ion may hold reactive groups within a substitution-inert complex, in proper array to facilitate a stereochemically selective multistep reaction. It is useful to refer to processes of this sort as *kinetic template reactions*, for the succession of reaction steps is determined by the metal ion. This technique has been utilized in these laboratories to close large rings.³⁰ The systems reported here constitute examples of a second class of template reaction.³¹ It appears highly likely that these systems involve sequestration of the product of an equilibrium which would, in the absence of the metal ion, go on to the formation of a different final product, as described earlier. This *equilibrium template reaction* essentially involves stabilization of an intermediate in a thermodynamically directed process. The scheme is illustrated



For the case in point, the alternative possibility might be suggested that the mercaptoamine (MEA) first complexes to the metal ion forming $\text{Ni}(\text{MEA})_2$, followed by reaction with the diketone to form the final product. However, the attempted reaction of bis-(mercaptoethylamino)-nickel(II) with 2,3-pentanedione reveals that this process is much slower than that employed in the syntheses of Ni(PE) and gives lower yields of the product ($\sim 10\%$).

One might also suspect that the thiazolidine forms and is then converted to the Schiff base by the action of the metal ion. However, again the alternate process proceeds much much more slowly if at all in this specific case.

It is quite probable that the very interesting cyclization reaction observed by Curtis and co-workers³²⁻³⁶ involves, successively, an equilibrium template reaction and a kinetic template reaction. The initial process probably involves Schiff base reactions between free amino groups and acetone, producing bis-acetone-ethylenediimine (BAE). This species may then be selectively coordinated and concentrated in this manner. The resulting complex may well be square-



planar in configuration and the action of the required free base should serve to abstract protons from the methyl group of the condensed acetone. This, in turn, may be viewed as facilitating an internal *kinetic template reaction* by means of which the aldol-like condensation occurs between adjacent acetone groups. Phenomena of these classes are expected to be of much

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significance in many processes that are metal ion dependent.

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Olefin Coordination Compounds of Rhodium: The Barrier to Rotation of Coordinated Ethylene and the Mechanism of Olefin Exchange

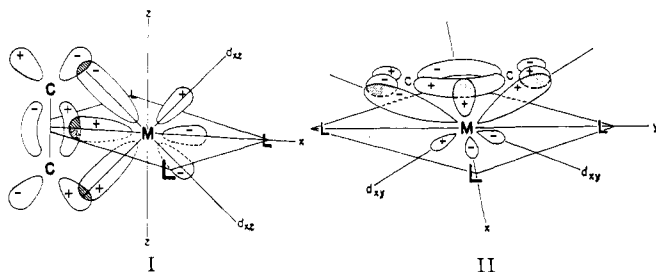
BY RICHARD CRAMER

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Coordinated olefins have generally been depicted as rigidly attached to metal ions with the olefin bond perpendicular to the coordination plane in 4-coordinate planar complexes. Nuclear magnetic resonance evidence is presented to show that ethylene coordinated to rhodium(I) in the compound $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ may rotate with the coordination bond as axis. The energy barrier to rotation is 6 kcal. Ethylene exchange with $(\text{CH}_3\text{COCHCOCH}_3)\text{Rh}(\text{C}_2\text{H}_4)_2$ is a bimolecular reaction. The difference in ability of $(\text{CH}_3\text{COCHCOCH}_3)\text{Rh}(\text{C}_2\text{H}_4)_2$ and $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ to undergo ethylene exchange is discussed in terms of the effective atomic number of rhodium in these compounds.

Introduction

Following Dewar¹ it has been customary² to describe the bond by which olefins are coordinated to transition metals as consisting of two parts (I): (a) a σ -bond, corresponding to the classical coordination bond, formed by overlap of the filled π -orbital of the olefin with a vacant metal orbital; and (b) a π -bond obtained through overlap of the vacant antibonding orbital of the olefin with a filled d -orbital of the metal.



X-Ray studies show that in crystalline $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$,^{3a} $[(\text{C}_2\text{H}_4)\text{Pt}(\text{HN}(\text{CH}_3)_2)\text{Cl}_2]$,^{3b} $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$,^{3c} and other platinum complexes,^{3d} the olefin double bond is perpendicular to the coordination plane as shown in I with the d_{xz} metal orbital involved in the π -bond. This geometry has been adopted generally for planar complexes containing olefins. However, it is also conceivable that the d_{xy} metal orbital could participate in a similar bond (II). It will be shown that the n.m.r. spectrum of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ indicates that in this compound coordinated ethylene molecules rotate with the coordination bond as axis. The low energy barrier to rotation (6 kcal.) suggests that a structure such as II is involved.

Mechanism for the Equilibration of Ethylene Protons in Bis(ethylene)- π -cyclopentadienylrhodium(I).—At 25° the proton n.m.r. spectrum of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ ⁴ dissolved in chloroform has three maxima (see Fig. 1), a sharp peak at -5.15 p.p.m. (relative to tetramethylsilane), attributed to cyclopentadienyl protons, and broad absorptions centered at -2.77 and -1.12

p.p.m. due to protons of coordinated ethylene. Integration of the absorption signal shows that the ratio of the three kinds of protons is 5:4:4. The peak at -5.15 p.p.m. is split into a doublet (separation 0.8 c.p.s.) by rhodium. When the solution of the complex is chilled to -20° , the absorptions at -2.77 and -1.12 p.p.m. are each split into two pairs of doublets. If the solution is heated to 57° , the ethylene proton absorption bands converge into a single absorption at -1.93 p.p.m., corresponding to rapid proton equilibration at that temperature. Since it is highly probable that the coordinated ethylene molecules of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ are equivalent, it appears that each ethylene ligand carries two protons of each type.

Several mechanisms may be considered for the equilibration of olefin protons in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$: (1) Individual protons may exchange without disturbing the rhodium-ethylene coordination bond. (2) Protons may exchange by a nonclassical tunneling mechanism. (3) Ethylene molecules may exchange by a mechanism involving dissociation. (4) Coordinated ethylene molecules may exchange in a bimolecular reaction of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ without dissociation of ethylene. (5) Depending upon the reason for nonequivalence of ethylene protons, rapid rotation of coordinated ethylene with either the olefin bond or the coordination bond as axis might lead to a single proton absorption.

These possible mechanisms have been assessed experimentally and the first four are excluded. It appears that rapid rotation with the coordination bond as axis is responsible for proton isomerization.

The first mechanism, exchange of olefin protons, was tested by heating solutions of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ in CH_3OD and it was found that no H-D exchange occurred under conditions of rapid ethylenic proton equilibration. This result was confirmed by the discovery that olefin protons of an analogous compound $\text{C}_5\text{H}_5\text{Rh}(\text{CH}_2=\text{CHCH}_2-\text{CH}=\text{CH}_2)$ do not equilibrate at 100° . It is expected that the chelated structure of this complex could interfere with proton equilibration by rotation or olefin dissociation mechanisms but not by a hydrogen exchange mechanism.

The possibility of a tunneling mechanism was excluded when deuterium n.m.r. studies showed that deuterium equilibration in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$ was substantially as fast as proton equilibration in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$.

In examining the possibility of ethylene exchange by a dissociation mechanism, it was found that no exchange of coordinated C_2H_4 and free C_2D_4 occurred in 5 hr. at 100° , conditions far more rigorous than those required for hydrogen equilibration of complexed ethyl-

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