ion of charge +2 is not eluted by 0.1 *M* perchloric acid.[5]) In an effort to establish correctly the absorbancy indices for the *trans* isomer, six experiments of the breakthrough type were performed. In four of these, portions of *trans* isomer (with a trace of *cis* isomer as contaminant) were poured through a short (~ 15 cm.) column; in the other two experiments, portions of solution containing ~ 75% *trans* isomer and ~ 25% *cis* isomer were used. Thirteen portions of the solution which came through initially were examined at 270 and 300 mμ where the relative absorbancies of the two isomers are rather different. The average value of A_{300}/A_{270} on ten of these portions was 1.31 ± 0.02.[10] Since the duration of these experiments was short enough that an insignificant amount of isomerization occurred and since the same result was obtained in an experiment in which 25% *cis* isomer was present, it will be assumed that the value $A_{300}/A_{270} = 1.31$ is characteristic of the *trans* isomer. The value of A_{300}/A_{270} for portions under the second peak in a typical ion-exchange run is 0.96. With this as the first approximation of the value of A_{300}/A_{270} characteristic of the *cis* complex, it can be estimated that the material coming off in the central part of the first elution peak with a value of $A_{300}/A_{270} = 1.30$ is contaminated to an extent of approximately 3% with the less easily eluted *cis* isomer. If it is assumed that the second elution peak is contaminated with 3% of the more easily eluted *trans* isomer, the value 0.95 is calculated to be the correct value of A_{300}/A_{270} for the *cis* isomer.

In Fig. 2 are presented the spectra of the two isomeric complexes. Certain features of these curves are of interest from a theoretical point of view. The two absorption bands in the visible region of the spectrum arise from transitions involving the d electrons of the chromium(III) atom and, presumably, can be explained by the application of crystal field theory to the complex.[11] This theory predicts a splitting of the lower energy transition which is not observed. This is due, no doubt, to the close similarity of water and thiocyanate ion with regard to their positions in a "spectrochemical" series.[12] It is observed, however, that the *cis* complexes with no center of symmetry has a slightly greater absorbancy as expected.[13]

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[10] Three of the portions did not come within reasonable limits of this average. Two of these deviating portions were from an experiment in which relatively pure *trans* isomer was used and the other was from an experiment on the 75–25% mixture.

[11] C. J. Ballhausen and C. K. Jorgensen, *Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.*, **29**, No. 14 (1955); L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

[12] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311, 316 (1956).

[13] F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

The Interaction of 2-Methyl-2-amino-3-butanone Oxime with Some Transition Metal Ions

BY R. KENT MURMANN

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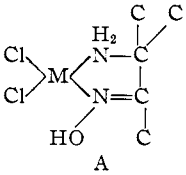
A new series of coördination compounds, formed with transition metal ions and 2-methyl-2-amino-4-butanone oxime, have been prepared. The reagent is not specific but forms stable compounds with most transition metal ions which are soluble in water and some organic solvents. With compounds having a coördination number of 4 or 6 the hydrogen bond is always formed and there is a tendency to force a *cis*-planar configuration on the molecules. The physical properties of these compounds will allow studies to be made on the effect of the hydrogen bond on stability and on the mechanism of substitution on non-ionic coördination compounds.

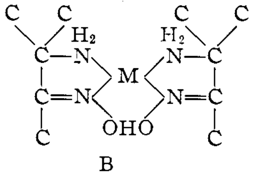
Introduction

It is well known that aliphatic *syn*-α-dioximes form coördination compounds with transition metal ions which contain strong hydrogen bonds[1] and that the organic ligand is often quite specific for a particular ion. Unfortunately the known compounds do not lend themselves to convenient study because of ease of hydrolysis and oxidation of the ligand and insolubility of the complexes. It was thought that a ligand capable of forming only one hydrogen bond when chelated would have more suitable properties. Thus in an effort to determine the inherent characteristics of the hydrogen bond in coördination compounds and to elucidate the mechanism of substitution reactions in nonaqueous solvents a new series of compounds have been prepared. This paper is the first of a series on this topic and presents the preparation and properties of coördination compounds of some transition metal ions with 2-methyl-2-amino-3-butanone oxime and its N-alkyl derivatives.

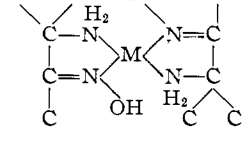
With metal ions having a planar configuration, Cu(II), Pd(II) and Pt(II) there are three types of compounds (ABC) which should be capable of existence. An effort has been made to produce each of these but only A and B have been isolated.



A



B



[1] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

The planar and octahedral configurations for Ni(II) have been established and it might be expected that under the proper conditions they could be formed with the amine–oxime type of ligand. If a strong hydrogen bond is formed the two amine–oxime rings must lie in the same plane which would necessitate either rearrangement or spanning of *trans* positions by the entering third ligand. Rearrangement would be expected to break the hydrogen bond while adding the third ligand across *trans* positions would result in considerable strain. Thus, a very strong hydrogen bond would tend to limit the maximum number of ligands attached to 2 resulting in either an octahedral structure with two waters in the *trans* positions or in a planar structure. The energy difference between these structures is quite small for ethylenediamine type ligands and interconversion can be made to take place by changing the anion, the solvent and by small changes in the organic ligand. In the amine–oxime series the strength of the metal to nitrogen bond should be great enough to reduce the attraction for the additional water molecules sufficiently to stabilize a planar dsp^2 hybridization.

Formation of compounds of the type $[Co(AO)_2\text{-}HX_2]^{0 \text{ to } +2}$ (where X may be a negatively charged or neutral molecule) should be possible by analogy with the dimethylglyoxime Co(III) series $[Co(DMG)_2\text{-}2H\ X_2]^{+1 \text{ to } -1}$. The non-ionic nature of some members of this series will permit studies (in progress) to be made on substitution reactions without the complication of ion-pair formation.

Experimental

Nitrosyl chloride was prepared by the method of Morton and Wilcox[2] and was redistilled until it had a boiling point of −4.5 to −5.5°.

2-Methyl-2-butene was prepared by dehydration of 2-methyl-2-butanol with sulfuric acid and upon fractional distillation had a boiling range of 37.8–39.0°, n_D 1.3852.[3]

2-Chloro-2-methyl-3-nitrosobutane was prepared by the action of nitrosyl chloride on an excess of anhydrous 2-methyl-2-butene at about −5°.

Eighty-seven ml. (123.5 g.) of nitrosyl chloride was distilled slowly into 500 g. of dry 2-methyl-2-butene whose temperature was maintained between −8 to −5° by means of an acetone–ice slurry. The solution became light blue and a white crystalline solid was deposited. After the addition was complete (3 hr.) the mixture was allowed to stand at −5° for two hours and cooled to about −20° with an acetone–Dry Ice slurry. The white solid was removed on a pre-cooled filter, washed several times with cold methanol and dried under vacuum; yield 167 g., m.p. (after recrys. from MeOH) 68–69°.[4]

Anal. Calcd. for $C_5H_{10}NOCl$: Cl, 26.17. Found: Cl, 26.22.

The preparation of 2-amino-2-methyl-3-butanone oxime was carried out by the action of anhydrous ammonia on 2-chloro-2-methyl-3-nitrosobutane.

One hundred grams of 2-chloro-2-methyl-3-nitrosobutane was added slowly to 1 l. of a saturated absolute methanol–NH_3 solution at 0°. The mixture was allowed to stand overnight at 0° and warmed at room temperature for 5 hr. With a continuous stream of NH_3 passing through the solution it was refluxed for 12 hr. Evaporation to dryness under vacuum (20–30°) produced a solid which was extracted with hot anhydrous benzene. The benzene extracts were evaporated under vacuum until crystallization occurred and then cooled. The product was collected on a filter, recrystallized from a mixture of benzene and petroleum ether and sublimed; yield 27 g., m.p. 98–98.5° (sublimes). *Anal.* Calcd. for $C_5H_{12}N_2O$: C, 51.65; H, 10.34; N, 24.15. Found: C, 51.48; H, 10.11; N, 24.42. The residue from the benzene extractions contained the main portion of the product as the hydrochloride. It was separated from NH_4Cl impurity by extraction with boiling *sec*-butyl alcohol, yield 47 g., m.p. 193–194°. *Anal.* Calcd. for $C_5H_{13}N_2OCl$: Cl, 23.24. Found: Cl, 23.18.

Analogous procedures were employed in the preparation of N-substituted amine–oximes using anhydrous alcoholic-aliphatic amine solutions. In these cases the yield of purified product was about 60% of theory. *Anal.* (*n*-PrAO·HCl).[5] Calcd. for $C_8H_{19}N_2OCl$: Cl, 18.24. Found: Cl, 18.30. (*n*-AmAO·HCl.) Calcd. for $C_{10}H_{23}N_2OCl$: Cl, 15.96. Found: Cl, 16.02. (DMAO·HCl.) Calcd. for $C_7H_{17}N_2OCl$: Cl, 19.66. Found: Cl, 19.52. (PhAO·HCl.) Calcd. for $C_{11}H_{17}N_2OCl$: Cl, 15.51. Found: Cl, 15.34.

The attempted preparation of 2,2′-ethylenediamino-bis-(2-methyl-3-butanone) dioxime by the action of excess 2-chloro-2-methyl-3-nitrosobutane on ethylenediamine produced a mixture from which the desired product could not be isolated. It was possible however to isolate the nickel-(II) complex of this ligand in pure state.

Palladium(II) Compounds. $[Pd(AO)Cl_2]^0$.—Palladium chloride (0.005 *M*) was dissolved in a solution containing 5 ml. of concd. HCl, 5 g. of KCl and 50 ml. of water. To this was added 0.01 mole of (AOHCl) dissolved in 15 ml. of water. Small portions of $NaHCO_3$ were added until the *p*H reached a value of about 4 and the solution was warmed to 60°. Orange-yellow crystals deposited and after cooling were collected on a filter. The product was recrystallized from an ethanol–water mixture; yield 77% of theory.

In an analogous manner $[Pd(n\text{-}PrAO)Cl_2]^0$, $[Pd(n\text{-}AMAO)Cl_2]^0$, $[Pd(DMAO)Cl_2]^0$ and $[Pd(AO)Cl_2]^0$ were prepared with yields ranging from 60 to 80% of theory.

$[Pd(AO)_2\text{-}H]Cl\cdot 2H_2O$.[6]—A mixture of 0.01 mole of $[Pd(AO)Cl_2]$, 0.015 mole of (AOHCl) and 100 ml. of water were heated to 90° on a steam-bath and very small portions of $NaHCO_3$ added until the solution was nearly colorless. The solution was passed through a filter to remove suspended particles and a portion of the solvent removed by boiling. The solution (about 40 ml.) was allowed to crystallize at 0° and the product collected on a filter; yield 55% of theory consisting of white plates with a slight yellow tinge.

On drying under vacuum the water of crystallization is lost and a white powder, $[Pd(AO)_2\text{-}H]Cl$, remains.

$[Pd(AO)_2\text{-}H]ClO_4$.—To 0.0053 mole of $[Pd(AO)_2\text{-}H]Cl\cdot 2H_2O$ dissolved in 10 ml. of water was added a solution of 0.0048 mole of $AgClO_4$ in 15 ml. of water. The mixture was warmed to 70° and the precipitated AgCl removed on a filter. On cooling the filtrate, yellowish-white crystals were deposited. Purification was accomplished by recrystallization from a small amount of water; yield 72% of theory.

Platinum(II) Compounds. $[Pt(AO)Cl_2]^0$.—A mixture of 0.01 mole of K_2PtCl_4, 0.02 mole of (AOHCl) and 30 ml. of H_2O was heated on a steam-bath and small portions of $NaHCO_3$ added to keep the *p*H between 3 and 4. After 24 hr. the solution became nearly colorless and the yellow crystals which were deposited were collected on a filter, washed with cold water and recrystallized from water containing a small amount of HCl; yield 87% of theory.

In the same manner $[Pt(n\text{-}PrAO)Cl_2]^0$ and $[Pt(n\text{-}AmAO)Cl_2]^0$ were prepared as yellow plates and needles, respectively. $[Pt(n\text{-}AmAO)Cl_2]^0$ has a tendency to be deposited as an oil from water solutions but crystals are obtained from an ethanol–water mixture. (Molecular weight of $[Pt(n\text{-}AmAO)Cl_2]^0$ by Rast method = 495. Calcd. =

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[2] J. R. Morton and H. W. Wilcox, "Inorganic Syntheses," Vol. IV, McGraw–Hill Book Co., New York, N. Y., 1953, p. 48.

[3] M. Michael and P. Zeidler, *Ann.*, **385**, 259 (1911).

[4] W. J. Hickenbottom, "Reactions of Organic Compounds," 2nd Ed., Longmans, Green, New York, N. Y., 1948.

[5] The ligands discussed here are designated as follows: (AO) = 2-amino-2-methyl-3-butanone oxime, (*n*-PrAO) = 2-*n*-propylamino-2-methyl-3-butanone oxime, (*n*-AmAO) = 2-*n*-pentylamino-2-methyl-3-butanone oxime, (DMAO) = 2-dimethylamino-2-methyl-3-butanone oxime, (PhAO) = 2-phenylamino-2-methyl-3-butanone oxime, (EnAO) = 2,2′-ethylenediamino-bis-(2-methyl-3-butanone) dioxime, (DMG) = dimethylglyoxime, (TetraMeEn) = 2,3-dimethyl-2,3-diaminobutane.

[6] The designation −H is meant to express the essentially complete ionization of an oxime hydrogen in the formation of a hydrogen bond.)

452.) Attempts to prepare $[Pt(DMAO)Cl_2]$ always resulted in reduction to platinum metal.

$[Pt(AO)(n\text{-}PrAO)\text{-}H]I$.—A mixture of 0.001 mole of $[Pt(n\text{-}PrAO)Cl_2]^0$, 0.002 mole of (AO) and 50 ml. of methanol were refluxed for 4 hr. All of the starting materials dissolved and the yellow color disappeared. The alcohol was removed under vacuum and 30 ml. of water added. This solution was saturated with NaI(s) and allowed to stand. Over a period of 8 hr. yellowish-white crystals were deposited which were recrystallized from a small amount of water; yield 55% theory.

Nickel(II) Compounds. $[Ni(AO)_2\text{-}H]I$.—Dilute NaOH solution was added to a mixture of 0.2 mole of (AOHCl) and 0.1 mole of $[Ni(H_2O)_6](NO_3)_2$ in 100 ml. of water until the *p*H remained at 7.0. The yellow solution was clarified by passing it through a filter and a large quantity of saturated NaI solution slowly added. After cooling, the yellow needles were collected and recrystallized from a methanol–ether mixture; yield 85% of theory.

The NO_3^- and ClO_4^- salts may be prepared from the iodide by treatment with a slight deficiency of the appropriate silver salt while the Cl^- and Br^- salts are best obtained by substituting NaBr or LiCl for NaI. All of the compounds are soluble in water and alcohol but insoluble in ether. They have one sharp absorption peak in the visible spectrum; molar absorbancy, $\epsilon_{\text{max.}}$ at 419 mμ = 132.

In a like manner $[Ni(n\text{-}PrAO)_2\text{-}H]Br$ ($\epsilon_{\text{max.}}$ at 426 mμ = 153) and $[Ni(n\text{-}AmAO)_2\text{-}H]Cl$ ($\epsilon_{\text{max.}}$ at 428 mμ = 156), are easily obtained.

$[Ni(DMAO)_2]Br_2$.—To a solution of 0.01 mole of $[Ni(H_2O)_6](NO_3)_2$ dissolved in 25 ml. of water was added 0.02 mole of (DMAO). A red color developed and the solution became essentially neutral. It was cooled to 5° and NaBr(s) added to saturation. After several hours the red crystalline product was collected and washed with a small quantity of cold water. It was recrystallized from warm water containing a large excess of NaBr; yield 35% of theory. The compound is soluble in water, extremely soluble in alcohol and forms a non-crystalline insoluble perchlorate salt; ($\epsilon_{\text{max.}}$ at 468 mμ = 176).

$[Ni(EnAO)\text{-}H]I$.—Fifty grams (0.37 mole) of 2-chloro-2-methyl-3-nitrosobutane was added to a cold solution of 150 ml. of absolute methyl alcohol and 9 g. (0.15 mole) of anhydrous ethylenediamine. The mixture was stirred at 5° for 3 hr., room temperature for 8 hr. and then refluxed for 18 hr. under anhydrous conditions. The small amount of ethylenediamine hydrochloride which precipitated was removed on a filter and the filtrate distilled to a volume of 100 ml. Attempts to isolate (EnAO-2HCl) failed. Addition of 35.5 g. (0.15 mole) of $[Ni(H_2O)_6]Cl_2$, 100 ml. of water and sufficient NaOH to increase the *p*H to 9 resulted in a yellow-green solution. This was clarified and an excess of NaI(s) added whereupon yellow needles of the product were deposited. After cooling the crude product was collected and separated from alkali halides and $[Ni(en)_3]I_2$ by crystallization from absolute methanol; yield 40% of theory.

$[Ni(EnAO)\text{-}H]ClO_4$ may be prepared by treatment of the iodide with slightly less than the calculated amount of neutral $AgClO_4$ solution followed by removal of AgI and crystallization from methanol. It forms greenish-yellow needles which are soluble in acetone, alcohol and water but insoluble in ether; molar absorbancy, $\epsilon_{\text{max.}}$ at 378 mμ = 310.

Copper(II) Compounds. $[Cu(AO)Cl_2]^0$.—To 15 ml. of a solution containing 0.01 mole of $CuCl_2$ was added 0.01 mole of (AOHCl). The dropwise addition of 5 *M* NaOH solution to a *p*H of 3.0 caused the formation of a deep blue color and a crystalline precipitate. After cooling, the product was collected and recrystallized from methanol containing a small amount of water; yield 55% of theory.

$[Cu(AO)_2\text{-}H]ClO_4 \cdot 2H_2O$.—A solution of 0.01 mole of $[Cu(H_2O)_4]ClO_4)_2$ in 20 ml. of H_2O was added to 0.025 mole of (AOHCl) dissolved in 25 ml. of H_2O. The mixture was warmed gently and NaOH solution (5 *M*) slowly added to a *p*H of 8.0. The product crystallized with difficulty upon the addition of $NaClO_4$(s) and was purified by recrystallization from methanol–water solution as purple-blue needles; yield 48% of theory.

$[Cu(n\text{-}PrAO)_2\text{-}H]ClO_4$ and $[Cu(n\text{-}AmAO)_2\text{-}H]ClO_4$ can be produced in an analogous fashion. They are dark green-brown and are only slightly soluble in water but very soluble in alcohol.

Silver(I) Compounds. $[Ag(AO)_2]NO_3$.—Silver nitrate (0.01 mole) was dissolved in 5 ml. of water and added to 0.022 mole of (AO) dissolved in 10 ml. of water. The solution was cooled to 5° and after 10 min. the colorless crystals collected on a filter and dried under vacuum. Recrystallization was accomplished by dissolving in a small amount of hot absolute methanol (some decomposition), removing the finely divided Ag by filtration through a hardened paper, cooling to −5° and adding redistilled ether dropwise. The colorless crystals were collected on a sintered glass filter, washed with ether and dried in the dark at 25° and 1 mm. pressure. The compound decomposes giving metallic silver on heating or exposure to light; yield 80% of theory. $[Ag(AO)_2]ClO_4$ was prepared in the same manner and is less soluble and more stable than the nitrate.

Cobalt(III) Compounds. $[Co(AO)_2\text{-}HCl_2]^0$.—A solution of $[Co(H_2O)_6]Cl_2$, 0.21 mole of (AOHCl) and 500 ml. of H_2O was treated with 0.27 mole of NaOH dissolved in 100 ml. of H_2O. Air was bubbled through the brown solution for 12 hr. and 100 ml. of concd. HCl added. The red solution was evaporated on a steam-bath to a volume of about 100 ml. After cooling, the fine green needles were collected on a filter, washed with cold water, ethanol and dried. Recrystallization was accomplished from a large amount of absolute methanol; deep green needles, soluble in H_2O, methanol and acetone, insoluble in ether; m.p. 185–195° dec.; yield 52% of theory ($X_m \equiv 107 \times 10^{-6}$).

In the same manner $[Co(AO)_2\text{-}H\ Br_2]^0$ may be prepared. It is more soluble and lighter in color than the chloro complex.

$[Co(AO)_2\text{-}H(NO_2)_2]^0$.—A mixture of 0.01 mole of $[Co(AO)_2\text{-}H\ Cl_2]^0$, 0.025 mole of $NaNO_2$ and 150 ml. of H_2O was warmed to 60° for 2 hr. Yellow crystals were deposited. After evaporation to about 40 ml. and cooling they were collected on a filter and recrystallized from methanol; yellow needles, soluble in H_2O, acetone–methanol; insoluble in ether; yield 80% of theory.

This compound may also be prepared directly from cobaltous nitrate by aerating slightly basic solutions containing 1/2.2/2.5/2.5 *M* ratio of Co(II), (AOHCl), $NaNO_2$ and NaOH, respectively. The yield based on Co(II) is about 85% of theory.

$[Co(AO)_2\text{-}H(NO_2)Cl]^0$.—A solution of 5 g. of $[Co(AO)_2\text{-}H(NO_2)_2]^0$ and 5 g. of NH_4Cl in 30 ml. of water was heated to 90° for about 8 hr. Dark red crystals were deposited and a gas (N_2) released. While still hot the product was collected on a filter, washed with cold water and dried. Purification was accomplished by solution in the minimum amount of hot water followed by cooling to 0° for about 36 hr.; yield 60% of theory.

$[Co(AO)_2\text{-}H(NO_2)Br]$ was prepared by substituting NH_4Br as the reactant.

$[Co(AO)_2\text{-}H(NO_2)(H_2O)]NO_3$.—A mixture of 1.0 g. of $[Co(AO)_2\text{-}H(NO_2)(Cl)]$, 0.50 g. of $AgNO_3$ and 10 ml. of water was ground for 4 hr. at room temperature. The mixture was heated to 60° for 1 hr. and the AgCl removed on a filter and extracted with hot water. The combined filtrates were evaporated under vacuum and the crystalline product collected and recrystallized from water as brown crystals which are soluble in water and alcohol; yield 75% of theory.

$[Co(AO)_2\text{-}H(SCN)_2]^0$.—Two grams of $[Co(AO)_2\text{-}HCl_2]^0$ was dissolved in 50 ml. of H_2O containing 3 g. of NaSCN. The solution was warmed to 90° for 10 min. and a red crystalline product deposited. Keeping the mixture at 80°, small amounts of methanol were added until solution was complete. On cooling, bright red needles were obtained. It was recrystallized from methanol–water solution and is soluble in alcohol and acetone but insoluble in chloroform and ether; yield 68% of theory.

$[Co(AO)_2\text{-}H(N_3)_2]$.—A solution of 2 g. of $[Co(AO)_2\text{-}HCl_2]$ and 3 g. of NaN_3 in 50 ml. of H_2O was warmed to 80° for 2 hr. The solution was evaporated to 20 ml. and allowed to crystallize for several days. The dark purple crystals were collected and recrystallized from a methanol–water mixture; very soluble in alcohol and water; yield 74% of theory.

The equivalent conductivity at a concentration of 9.76×10^{-4} *M*, Λ_{1024}, was determined at 25°. $[Co(AO)_2\text{-}H(NO_2)_2]^0$; $\Lambda_{1024} = 0.2$, $[Co(AO)_2\text{-}H(SCN)_2]^0$; $\Lambda_{1024} = 0.0$, $[Ni(EnAO)\text{-}H]ClO_4$; $\Lambda_{1024} = 98$, $[Ni(AO)_2\text{-}H]ClO_4$; $\Lambda_{1024} = 104$, $[Pt(AO)Cl_2]^0$; $\Lambda_{1024} = 2.3$, $[Ni(TetraMeen)_2](NO_3)_2$; $\Lambda_{1024} = 197$. Comparison with known values for similar compounds[7]

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(7) Hein and Franz, "Chemische Koördinations Lehre," S. Hirzel Verlag, Leipzig, 1950, p. 6.

TABLE I

ANALYSIS OF COMPOUNDS

Compound	Calcd. Metal	Calcd. C	Calcd. H	Calcd. N	Calcd. Anion	Found Metal	Found C	Found H	Found N	Found Anion
$[Pd(AO)Cl_2]$	36.3	20.48	4.07	9.54		36.9	20.56	4.03	9.48	
$[Pd(AO)_2\text{-}H]ClO_4$	23.8	26.74	5.12	12.47		23.6	26.51	5.14	12.42	
$[Pd(n\text{-}PrAO)Cl_2]$	31.6	28.60	5.35	8.34		31.5	28.48	5.36	8.64	
$[Pt(AO)Cl_2]$	46.0	22.60	4.24	6.61	16.17	46.1	22.57	4.38	6.48	15.99
$[Pt(AO)(n\text{-}PrAO)\text{-}H]I$	32.8	26.22	4.88	9.41	21.34	32.7	26.26	4.93	9.38	21.59
$[Ni(AO)_2\text{-}H]I$	14.06	28.79	5.52	13.42	30.42	14.01	28.72	5.70	13.32	30.52
$[Ni(n\text{-}PrAO)_2\text{-}H]Cl$	14.36	46.95	8.56	13.70	8.68	14.37				8.91
$[Ni(DMAO)_2]Cl_2$	14.07	40.21	7.66	13.40	16.98	13.98				17.04
$[Ni(EnAO)\text{-}H]I$	13.27	32.59	5.66	12.66	28.73	13.41	32.63	5.58	12.71	28.51
$[Cu(AO)Cl_2]$	25.39	23.95	4.79	11.17	28.35	24.82	24.75	4.99	11.65	28.99
$[Cu(AO)_2\text{-}H]Cl$		36.39	6.97	16.98			36.24	6.81	16.99	
$[Co(AO)_2\text{-}H]Cl_2$	16.31	33.23	6.37	15.52	19.64	16.38	33.28	6.31	15.47	19.61
$[Co(AO)_2\text{-}H(NO_2)_2]$	15.42	31.41	6.02	21.99		15.49	31.62	5.99	21.88	
$[Co(AO)_2\text{-}H(NO_2)Cl]$		32.38	6.20	18.88			32.40	6.36	19.05	
$[Co(AO)_2\text{-}H(H_2O)_2](ClO_4)_2$	11.21					11.30				
$[Co(AO)_2\text{-}H(NO_2)(H_2O)](NO_3)$		30.00	6.25	21.00			28.72	6.22	20.20	
$[Ag(AO)_2]NO_3$	26.76	29.9	5.99	17.49	15.48	25.70	28.94	6.02	16.64	14.35

leads to the conclusion that the substances behave in accordance with their provisional structure.

The infrared absorption spectra were obtained on KBr-complex compressed disks with a Perkin–Elmer model 21 instrument and a sodium chloride prism.

Analyses for C, H and N were conducted by Galbraith Laboratories, Knoxville 17, Tenn.; for metals, halogens, etc., by standard procedures.

Discussion

In solution, the reaction of Cu(II) and Ni(II) with (AO) gives rise to a complex ion having a maximum of two ligands per metal ion as shown by Fig. 1. Since the analytical data (Table I), and conductivity indicate that the charge on these bis complexes is +1 it is probable that a hydrogen bond is formed with the release of a proton. Titration of solutions containing a 2/1 molar ratio of (AOHCl) to M^{+2} with OH^- show end-points corresponding to 3 ± 0.06 equivalent of OH^- consumed per mole of M^{+2} during complex formation, substantiating the strong acid character of $[M(AO)_2]^{+2}$.

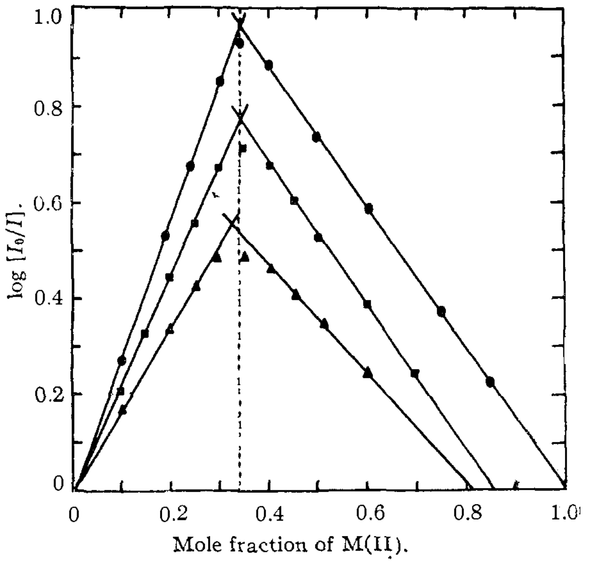

Fig. 1.—Continuous variation studies: ●, Ni(II) and (AO), pH 8.05, 420 mμ; ■, Cu(II) and (AO), pH 7.90, 520 mμ; ▲, Ni(II) and (DMAO), pH 9.0, 470 mμ.

It has been shown[8] that the formation of a hydrogen bond leads to the appearance of a weak band in the infrared region. Figure 2 shows the characteristic absorption in the 5–6 μ region and bis-dimethylglyoximenickel(II) is given for comparison. Thus it seems clear that in neutral or slightly alkaline solution and in the solid state the principal species contains a strong hydrogen bond.

There is a major difference in the behavior of the two metal ions toward (AO). Copper(II) reacts in a stepwise fashion being primarily in the form $[Cu(AO)(H_2O)_{2-4}]^{+2}$ in solutions of moderate acidity (pH 2.5–3.5) and high Cu/AO ratios while the predominant species is $(Cu(AO)_2-H]^{+1}$ in nearly neutral solutions (pH 5–9) and low Cu/AO ratios. This can be shown by the rather large shift in the maximum absorption frequency by varying the pH and metal to ligand ratio (Fig. 3). This is not the case with Ni(II) which does not form the mono-complex to any appreciable extent. Varying the pH or the Ni/AO ratio results only in a change in peak height (Fig. 3). Since the mono-complex would almost certainly absorb in the same general region as $[Ni(en)(H_2O)_4]^{+2}$, the presence of this species would easily be detected. It should be noted that even at high pH's and a AO/Ni ratio of 4 no shift in the absorption maximum was observed indicating the inability of the third ligand to be attached. The fact that the addition of the second ligand molecule has a larger formation constant than the first is not without precedent.[9] In certain highly carbon substituted ethylenediamines, Ni(II) forms only the yellow diamagnetic bis complex. This has been explained on the basis of a change from the sp^3d^2 to the dsp^2 hybridization on the addition of the second organic molecule. Certainly this change also occurs in $[Ni(AO)_2-H]^{+1}$ for it is diamagnetic ($X_m = -158 \times 10^{-6}$).

A comparison of (n-PrAO) and (n-AmAO) with the unsubstituted ligand shows a decrease in stabil-

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(8) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

(9) F. Basolo, Yun Ti Chen and R. Kent Murmann, THIS JOURNAL, **76**, 956 (1954).

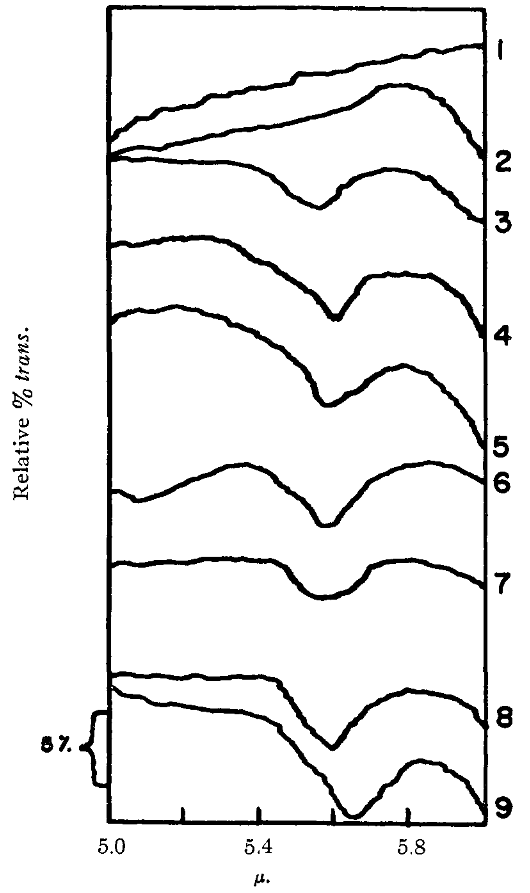


Fig. 2.—Infrared spectra: 1, $[Pt(AO)Cl_2]^0$; 2, $[Ni(DMAO)_2]Br_2$; 3, $[Ni(AO)_2\text{-}H](ClO_4)$; 4, $[Cu(AO)_2\text{-}H](ClO_4)$; 5, $[Pd(AO)_2\text{-}H]Cl$; 6, $[Pt(AO)(n\text{-}PrAO)\text{-}H]I$; 7, $[Co(AO)_2\text{-}H(NO_2)_2]^0$; 8, $[Co(AO)_2\text{-}HCl_2]^0$; 9, $[Ni(DMG)_2\text{-}2H]^0$.

ity due to steric hindrance between the alkyl groups. Since it is possible for the alkyl groups to be on opposite sides of the plane of the molecule, the stability decrease is small. The energy derived from the formation of a hydrogen bond is great enough to force a *cis*-configuration in spite of the interaction of the alkyl groups.

Molecular models indicate a tremendous strain in *cis*-$[Ni(DMAO]_2-H]^{+1}$. Figure 1 shows that the ratio of DMAO/Ni is 2 and the analytical data and infrared absorption (Fig. 2) give no indication of a hydrogen bond. In addition the formation takes place in a stepwise fashion lending support for steric hindrance and probably results in the *trans* form. It has been noticed however that a solution of the complex changes from red (max. absorption 468 mμ) to yellow (max. absorption 434 mμ) on aging several days. This form has not been isolated.

The addition of excess acid to all Cu(II) complexes results in immediate and complete decomposition to the aquated Cu(II) ion. $[Cu(AO)_2-H]^{+1}$ is unstable in warm, alkaline solutions and slowly precipitates Cu_2O (X-ray powder analysis) with the formation of 2,2,3,5,5,6-hexamethyl-2,5-dihydropyrazine[10] (m.p. 64–65°) and NH_3.

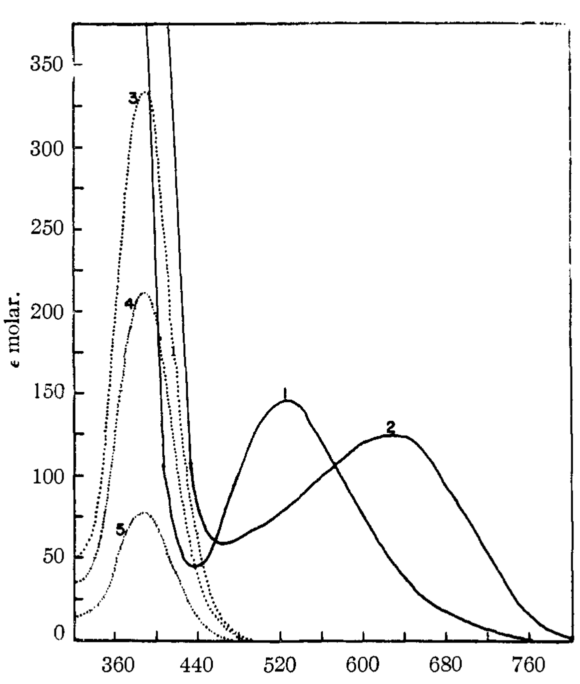
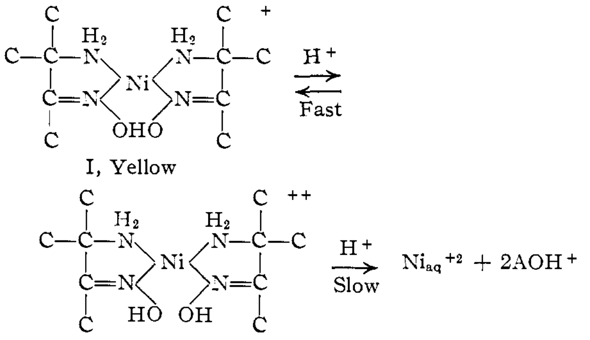


Fig. 3.—Absorption spectra, ——— copper(II) and (AO), $pH = 8.0$: 1, AO/Cu = 2; 2, AO/Cu = 1; - - - - Nickel(II) and (AO), $pH = 8.0$; 3, AO/Ni = 2; 4, AO/Ni = 1.25; 5, AO/Ni = 0.50.

$[Ni(AO)_2-H]^{+1}$, $[Ni(EnAO)-H]^{+1}$ and the mono-alkyl substituted complexes react with H^+ immediately forming a deep blue color similar to that of $[Ni(en)_2(H_2O)_2]^{+2}$. Gradually the blue color changes to the green of $Ni(II)_{aq}$. The reactions involved appear to be



Quantitative determinations which substantiate these conclusions will be given in a subsequent paper. The slow reaction of diamagnetic ammine complexes of Ni(II) has been noted[9] previously and can be attributed to the filled 3d shell. It is interesting to note that the intermediate (II) is blue in color which for ethylenediamine type complexes indicates paramagnetism but it is not instantaneously labile.

$[Ag(AO)_2]^{+1}$ is difficult to obtain pure because of thermal and light sensitivity. It appears that chelation is not possible due to the coördination number of 2 and to the usual linear nature of the sp orbitals. This results in coördination of two (AO) groups through the amino-nitrogens. That the

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[10] S. Gabriel, *Ber.*, **44**, 64 (1911).

silver is in the +1 oxidation state is shown by its diamagnetism ($X_m = -194 \times 10^{-6}$). Stabilization of Ag(II) by (AO) should occur, for the structure would be planar and have the extra energy of the hydrogen bond. However, treatment with H_2O_2 or $S_2O_8^{=}$ does not appear to oxidize $[Ag(AO)_2]^{+1}$.

Palladium(II) in dilute acid solution rapidly forms compounds of the type $[Pd(AO)Cl_2]^0$ with all of the (AO)'s studied. In neutral media a second ligand is added which predominantly attaches *cis*. It has been shown[11] that $[Pd(AO)_2-H]ClO_4$ and $[Ni(AO)_2-H]ClO_4$ are isomorphous with one axis of the former's unit cell slightly enlarged. Platinum(II) slowly forms the intermediate $[Pt(AO)Cl_2]^0$ in acid solution and in neutral solution $[Pt(AO)_2\text{-}H]^{+1}$ may be isolated. In this case, however, the yield of the *cis* form is low and the *trans* may be present but difficult to isolate. In every Pt(II) or Pd(II) compound containing two (AO) groups the characteristic infrared absorption of the hydrogen bond was observed, and was absent in all mono-chelated complexes.

The action of free (AO) on $[Co(H_2O)_6](ClO_4)_2$ in water lowers the *p*H and yields a slightly soluble brown precipitate of $[Co(AO)_2-H]ClO_4$ which oxidizes rapidly with air to give a mixture of Co(III) compounds. The octahedral coördination compounds of Co(III) can be prepared using essentially the same procedures as for the corresponding ethylenediamine compounds. However, unlike the ethylenediamine and (DMG) compounds there is no evidence that a tris-(AO) compound exists and *p*H changes do not rupture the hydrogen bond as they appear to do in the $[Co(DMG)_2-2H\ X_2]^{-1}$ series.

The properties of the cobalt-(AO) compounds suggest that the (AO)'s have a planar configuration and that the monodentate ligands assume *trans* positions. Sterically, the formation of a hydrogen bond would appear to be impossible if this were not the case. In addition the green color of $[Co(AO)_2-HCl_2]^0$ is similar to many other *trans*-dichloro Co(III) compounds as opposed to the purple *cis* isomers. Attempts to prepare *cis* isomers by procedures analogous to those used in the ethylenediamine series have been unsuccessful.

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STORRS, CONNECTICUT

[11] L. Katz and M. Kay, private communication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, AND THE DIVISION OF MINERAL TECHNOLOGY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Dissociation Pressures of the Tantalum Silicides[1,2]

BY CLIFFORD E. MYERS AND ALAN W. SEARCY

RECEIVED AUGUST 27, 1956

The dissociation pressures of the tantalum silicides have been measured by the Knudsen effusion method. Phase modifications in the temperature ranges covered were established by quenching experiments and X-ray diffraction investigation. The heats of dissociation were combined with the heat of vaporization of silicon to obtain, for the heats of formation per silicon atom at 298°K.: $4.5TaSi_{0.22_2\pm0.03}$, −34.4 kcal.; Ta_2Si, −29.3 kcal.; $1.67TaSi_{0.60\pm0.08}$, −26.7 kcal.; and $\frac{1}{2}TaSi_2$, −11.6 kcal.

The silicides of tantalum[3-5] have been shown by Kieffer, Benesovsky, Nowotny and Schachner[6] to have melting points in excess of 2000°. From a consideration of the trends in stability of carbides, nitrides and other related compounds as well as from stabilities demonstrated in high temperature chemical reaction,[7] the silicides of tantalum could be predicted to be among the most stable of all silicides from a thermodynamic standpoint. Because of the expected high stabilities, measurement of heats and free energies of formation of the tantalum silicides seemed of particular interest. Accordingly, stabilities of all four of the stable tantalum silicide phases: $TaSi_{0.22_2\pm0.03}$, Ta_2Si, $TaSi_{0.60\pm0.08}$ and $TaSi_2$ have been determined from Knudsen effusion[8] measurements of the silicon dissociation pressures by means of apparatus and techniques outlined by Searcy and McNees.[9] (A fractional formula such as $TaSi_{0.22_2}$ or $TaSi_{0.60}$ is used when the ideal structure is unknown, or when there is evidence that the actual structure may be different from the ideal. For Ta_2Si and $TaSi_2$ the actual phase compositions apparently are those corresponding to ideal crystal structures.) A high temperature quenching furnace was used to determine which modifications of the various phases were stable in the temperature range of the dissociation pressure measurements.

Phase Studies

A $TaSi_2$ phase has been known for many years.[3,4] Additional tantalum silicides of compositions $TaSi_{0.22_2\pm0.03}$, Ta_2Si and $TaSi_{0.60\pm0.08}$ were more recently reported both by Brewer, Searcy, Templeton and Dauben[5] and by Nowotny, Schachner, Kieffer

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[1] From a thesis by Mr. Myers in partial fulfillment of the requirements for the Ph.D. degree at Purdue University.

[2] This research was supported by the Office of Naval Research.

[3] O. Hönigschmid, *Monatsh.*, **28**, 1017 (1907).

[4] H. J. Walbaum, *Z. Metallkunde*, **33**, 378 (1941).

[5] L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).

[6] R. Kieffer, F. Benesovsky, H. Nowotny and H. Schachner, *Z. Metallkunde*, **44**, 242 (1953).

[7] L. Brewer and O. Krikorian, *J. Electrochem. Soc.*, **103**, 38 (1956).

[8] M. Knudsen, *Ann. Physik*, [4] **28**, 999 (1909).

[9] A. W. Searcy and R. A. McNees, Jr., THIS JOURNAL, **75**, 1578 (1953).