In the solid state the complexes $[NiL_4X_2]$ lose lutidine on heating. In this way we have obtained in a pure state the compound $[Ni(3,4\text{-}L)_2Br_2]$, and the preparation of other compounds of this type is in progress. The blue-violet $[Ni(3,4\text{-}L)_2Br_2]$ closely resembles the corresponding complexes of 2,3- and 2,4-lutidine. Its magnetic moment, as well as its electronic spectrum, is consistent with a pseudo-tetrahedral configuration, only slightly distorted from the true T_d symmetry. Thus octahedral, tetrahedral, and square-planar configurations can be obtained for the complexes of nickel(II) salts with 3-substituted lutidines, depending on the anion, the lutidine ligand, and the physical state of the complex.

Acknowledgment.—This investigation was supported in part by the U. S. Atomic Energy Commission.

Contribution from the University of Michigan, Ann Arbor, Michigan,
and The Polytechnic Institute of Brooklyn, Brooklyn, New York

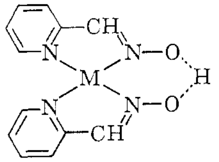
Some Homo- and Heteropolynuclear Chelates

By CHUI FAN LIU and C. H. LIU

Received October 15, 1963

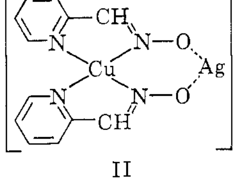
The complex compounds *cis*-bis(pyridine-2-aldoxime)copper(II), -palladium(II), and -platinum(II) themselves have been successfully used as coordinating agents. They behave as oxygen-donor bidentate ligands in forming metal chelates. Homopolynuclear chelates and heteropolynuclear chelates have been prepared containing one, two, or three of these "metal-complex" chelating agents.

Previous investigations[1-3] showed that square-planar complexes of pyridine-2-aldoxime were capable of intramolecular hydrogen bonding in the following type of structure.



I

It seems reasonable that in this type of structure, the oximate oxygens are so situated that other cations may substitute for the hydrogen ion to form regular metal coordination compounds. Potentiometric measurements have shown the existence of the following Cu(II)–Ag(I) heteropolynuclear chelate.[4]



II

The present investigation is concerned with the ability of complexes with this type of structure to coordinate with other metal ions to form isolable homo- and heteropolynuclear chelates.

Experimental

Homopolynuclear Chelates. Bis[bis(pyridine-2-aldoxime)copper(II)]copper(II) Perchlorate.—Pyridine-2-aldoxime was obtained from Aldrich Chemical Company, Milwaukee, Wis., and used without further purification. An aqueous solution of 1.70 g. (0.01 mole) of cupric chloride dihydrate in about 50 ml. was treated with 2.44 g. (0.02 mole) of pyridine-2-aldoxime dissolved in the stoichiometric volume of 0.1 *F* sodium hydroxide (1:1 by mole). The dark green solution was filtered, and solid sodium perchlorate was added. A crystalline precipitate formed which was filtered out, washed with distilled water, and air dried. *Anal.* Calcd. for $[Cu(C_6H_5N_2O)_2]_2Cu(ClO_4)_2$: C, 32.97; H, 2.29; N, 12.82. Found: C, 32.64; H, 2.28; N, 12.75. The same compound was obtained when dihydrogen bis(pyridine-2-aldoxime)copper(II) sulfate[2] was neutralized with sodium hydroxide (1:2 by mole) and sodium perchlorate was added to the resulting solution.

The iodide of this homopolynuclear chelate was prepared in the same manner as the perchlorate. *Anal.* Calcd. for $[Cu(C_6H_5N_2O)_2]_2CuI_2$: C, 31.10; H, 2.16; N, 12.10. Found: C, 31.53; H, 2.29; N, 12.49.

Bis[bis(pyridine-2-aldoxime)copper(II)]copper(II) Sulfate.—A solution of 4.57 g. of dihydrogen bis(pyridine-2-aldoxime)copper(II) sulfate trihydrate[2] in about 50 ml. was neutralized with the stoichiometric amount of 1 *F* sodium hydroxide. The resulting solution was evaporated on a steam bath to a very small volume, and about 100 ml. of methanol was added, followed by the addition of about 200 ml. of dioxane. Upon slow evaporation at room temperature, crystals formed. These were filtered out, washed with dioxane and then ether, and air dried. *Anal.* Calcd. for $[Cu(C_6H_5N_2O)_2]_2CuSO_4\cdot 3H_2O$: C, 34.99; H, 3.13; N, 13.62. Found: C, 34.10; H, 3.16; N, 13.98.

Dichloro[bis(pyridine-2-aldoxime)copper(II)]copper(II).—An aqueous solution of 1.70 g. of cupric chloride dihydrate in about 50 ml. was treated with 2.44 g. of pyridine-2-aldoxime dissolved in the stoichiometric volume of 0.1 *F* sodium hydroxide. Upon the addition of excess sodium chloride, a green precipitate formed which was filtered out, washed with distilled water, and air dried. *Anal.* Calcd. for $[Cu(C_6H_5N_2O)_2]CuCl_2\cdot H_2O$: C, 31.51;

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[1] C. F. Liu and C. H. Liu, *Inorg. Chem.*, **2**, 706 (1963).
[2] C. H. Liu and C. F. Liu, *J. Am. Chem. Soc.*, **83**, 4169 (1961).
[3] C. H. Liu and C. F. Liu, *ibid.*, **83**, 2615 (1961).
[4] C. H. Liu and C. F. Liu, *ibid.*, **83**, 4167 (1961).

H, 2.63; N, 12.25. Found: C, 31.79; H, 2.90; N, 12.02.

Neutralization of Monohydrogen Bis(pyridine-2-aldoxime)copper(II) Chloride and Dihydrogen Bis(pyridine-2-aldoxime)copper(II) Sulfate.—An aqueous solution of 3.41 g. of monohydrogen bis(pyridine-2-aldoxime)copper (II) chloride[2] in about 60 ml. was neutralized with the stoichiometric volume of 0.1 *F* sodium hydroxide. Evaporation of the resulting solution to a small volume at room temperature yielded green crystals. These were filtered out, washed with small portions of water, and air dried. *Anal.* Calcd. for $[Cu(C_6H_5N_2O)_2]_2Cu(OH)_2 \cdot 1.5H_2O$: C, 33.48; H, 3.49; N, 13.02. Found: C, 33.30; H, 3.35; N, 12.79. Neutralization of dihydrogen bis(pyridine-2-aldoxime)copper(II) sulfate[2] with 0.1 *F* sodium hydroxide in 1:1 mole ratio yielded the same compound. The identical compound was also obtained when cupric chloride was treated with an equimolar quantity of pyridine-2-aldoxime dissolved in the stoichiometric volume of 0.1 *F* sodium hydroxide. When this compound was dissolved in water and excess sodium chloride added, crystals formed which proved to be dichloro[bis(pyridine-2-aldoxime)copper(II)]copper(II).

Heteropolynuclear Chelates. [Bis(pyridine-2-aldoxime)palladium(II)]silver(I) Nitrate.—A sample of *trans*-bis(pyridine-2-aldoxime)palladium(II) dihydrate[1] was suspended in a solution of excess silver nitrate, and the mixture was heated on a steam bath for about 1 hr. The crystals changed from a light yellow to a brownish yellow color. After cooling to room temperature, the solid was filtered and washed with ice cold distilled water and air dried. *Anal.* Calcd. for $[Pd(C_6H_5N_2O)_2Ag]NO_3$: C, 27.67; H, 1.93; N, 13.29. Found: C, 27.70; H, 2.02; N, 13.11.

Dichloro[bis(pyridine-2-aldoxime)palladium(II)]copper(II).—*trans*-Bis(pyridine-2-aldoxime)palladium(II) dihydrate[1] was suspended in a solution of excess cupric chloride. The mixture was heated on a steam bath for 5 hr., during which time the crystals turned from a bright yellow to a greenish yellow color. The crystals were filtered out, washed with ice cold distilled water, and air dried. *Anal.* Calcd. for $Pd(C_6H_5N_2O)_2CuCl_2$: C, 29.88; H, 2.08; N, 11.61. Found: C, 29.73; H, 2.21; N, 11.51.

[Bis(pyridine-2-aldoxime)platinum(II)]silver(I) Nitrate.—The same procedure was used as in the preparation of the palladium analog, except in this case a sample of freshly precipitated *cis*-bis(pyridine-2-aldoxime)platinum(II) dihydrate[3] was used. *Anal.* Calcd. for $[Pt(C_6H_5N_2O)_2Ag]NO_3$: C, 23.72; H, 1.64; N, 11.53. Found: C, 23.55; H, 1.60; N, 11.41.

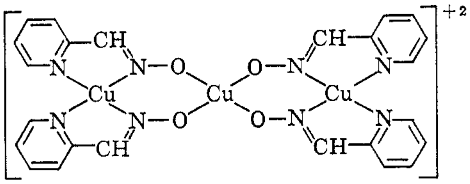
Dichloro[bis(pyridine-2-aldoxime)platinum(II)copper(II).—A sample of freshly prepared *cis*-bis(pyridine-2-aldoxime)platinum(II) dihydrate[3] was added to a solution of excess cupric chloride. A dark red solution resulted. On prolonged standing (several weeks) yellow crystals formed while the solution became green in color. The crystals were filtered, thoroughly washed with water, and air dried. *Anal.* Calcd. for $Pt(C_6H_4N_2O)_2CuCl_2$: C, 25.22; H, 1.76; N, 9.81. Found: C, 25.77; H, 1.96; N, 10.20.

Bis[bis(pyridine-2-aldoxime)platinum(II)]copper(II) Sulfate.—A solution of 0.473 g. of monohydrogen bis(pyridine-2-aldoxime)platinum(II) chloride[3] in 40 ml. of water was treated with 0.125 g. of cupric sulfate pentahydrate. The pH of the resultant solution was brought up to 9 by the addition of 0.1 *F* sodium hydroxide. A yellow precipitate formed which was filtered out, washed with distilled water, and air dried. *Anal.* Calcd. for $[Pt(C_6H_5N_2O)_2]CuSO_4 \cdot 7H_2O$: C, 24.82; H, 2.93; N, 9.65. Found: C, 24.70; H, 2.90; N, 9.51.

Tris[bis(pyridine-2-aldoxime)platinum(II)]rhodium(III) Perchlorate.—To a solution of 1 g. of rhodium trichloride trihydrate in 150 ml. of water was added 5.4 g. of monohydrogen bis(pyridine-2-aldoxime)platinum(II) chloride.[3] The pH of the solution was adjusted to a value of 4 with the addition of 0.1 *F* sodium hydroxide, and the reaction mixture was heated on a steam bath. The pH of the solution gradually dropped to a lower value. After about 1 hr., more sodium hydroxide was added to bring the pH to 4 again, and the mixture was again heated on the steam bath. The process was repeated at intervals. After 2 days, the pH of the solution no longer decreased. The solution was concentrated to about one-fourth of its original volume, and solid sodium perchlorate was added. The brown precipitate formed was filtered out, washed with water, and air dried. *Anal.* Calcd. for $[Pt(C_6H_5N_2O)_2]_3Rh(ClO_4)_3H_2O$: C, 24.99; H, 1.85; N, 9.72. Found: C, 25.13; H, 1.91; N, 9.74. Tris[bis(pyridine-2-aldoxime)platinum(II)]rhodium(III) bromide and tris[bis(pyridine-2-aldoxime)platinum(II)]rhodium(III) iodide were obtained in the same manner by the addition of sodium bromide and sodium iodide, respectively. *Anal.* Calcd. for $[Pt(C_6H_5N_2O)_2]$-$RhBr_3 \cdot 7H_2O$: C, 24.27; H, 2.47; N, 9.44. Found: C, 23.96; H, 2.41; N, 9.40. Calcd. for $[Pt(C_6H_5N_2O)_2]_3RhI_3 \cdot 4H_2O$: C, 23.15; H, 2.04; N, 9.00. Found: C, 23.03; H, 2.16; N, 9.11.

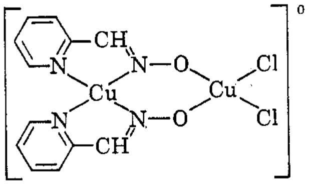
Discussion

Complexes of structure I are good chelating agents. The homopolynuclear chelates of copper(II) are easily prepared. The complex can be isolated as the perchlorate, iodide, or sulfate.



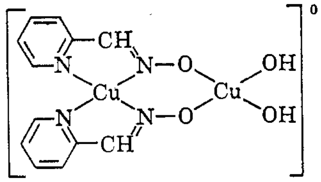
III

With excess chloride, the species isolated most likely has the structure



IV

Under the conditions of neutralization of dihydrogen bis(pyridine-2-aldoxime)copper(II) sulfate and monohydrogen bis(pyridine-2-aldoxime)copper(II) chloride, a compound is obtained which probably has the structure



When V is dissolved in water and excess chloride ion is added, IV is isolated. Various homopolynuclear chelates of copper(II) probably exist and are at equilibrium in solution, and the product isolated is determined by their relative solubilities.

The polynuclear compounds of bis(pyridine-2-aldoxime)palladium(II) and bis(pyridine-2-aldoxime)platinum(II) differ from the corresponding copper(II) compounds in that they are much less labile. While neutralization of dihydrogen and monohydrogen compounds of copper(II) yields homopolynuclear chelates, neutralization of either the monohydrogen bis(pyridine-2-aldoxime)palladium(II) ion or the platinum-

(II) analog results in the inner complex.[1,3] In addition, *cis–trans* isomerism is observed for the inner complex of platinum(II).[3] Due to the stable nature of the platinum(II) and palladium(II) complexes, heteropolynuclear chelates can be prepared. The silver(I) heteropolynuclear chelates with platinum(II) and palladium(II) have the same structure as the copper(II) compound (structure II), as indicated by their virtually identical infrared spectra. The action of excess cupric chloride on either *trans*-bis(pyridine-2-aldoxime)palladium(II) or *cis*-bis(pyridine-2-aldoxime)platinum(II) yields a compound with a structure completely analogous to the structure of the copper(II) compound (structure IV). Again the virtually identical infrared spectra of these compounds indicate that such is the case. Coordination of two bis(pyridine-2-aldoxime)platinum(II) molecules to each copper(II) ion yields the heteropolynuclear chelate whose structure is analogous to that of the homopolynuclear chelate of copper(II) (structure III). The infrared spectrum of bis[bis(pyridine-2-aldoxime)platinum(II)]copper(II) perchlorate and that of the corresponding homopolynuclear copper(II) compound are essentially identical.

The method used to prepare the tris[bis(pyridine-2-aldoxime)platinum(II)]rhodium(III) ion is similar to the one used by Dwyer and Sargeson[5] to prepare the trisacetylacetone rhodium(III) complex. The formation of the heteropolynuclear chelate is considerably slower than the formation of the acetylacetone complex. The structure of this interesting heteropolynuclear chelate is probably that of a regular octahedral complex.

[5] F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953)

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan

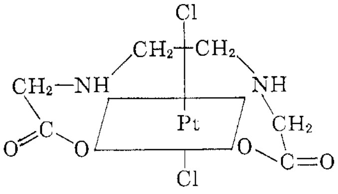
Complexes of Ethylenediamine-N,N′-diacetic Acid and Platinum. *cis*-Oxidation

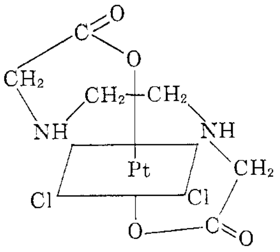
By CHUI FAN LIU

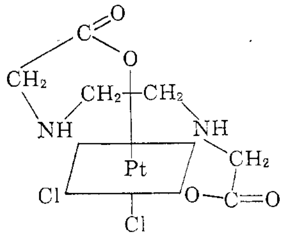
Received November 6, 1963

The complexes of ethylenediamine-N,N′-diacetic acid and platinum were studied. The ligand formed bidentate and tetradentate complexes with platinum(II). With platinum(IV) tridentate and tetradentate complexes were obtained. Oxidations of the platinum(II) complexes to form the dichloro(ethylenediamine-N,N′-diacetato)platinum(IV) were carried out. It was found that the regular type of addition reaction could be performed to yield the *trans*-dichloro isomer. It is of interest that the *cis*-dichloro isomer could also be obtained either by a ring closure reaction or by direct oxidation with the hexachloroplatinate(IV) ion.

The chelating ability of ethylenediamine-N,N′-diacetic acid was first investigated by Chaberek and Martell,[1] who measured the stability constants of several divalent metal ion complexes of this ligand. The complexes investigated, however, were of the labile type. No products were isolated and the structural aspects of the complexes were not examined. The present investigation is concerned with the nonlabile complexes between ethylenediamine-N,N′-diacetic acid and platinum(II), and the oxidation of the platinum(II) complexes to platinum(IV) compounds. The stereochemistry of this oxidation is of particular interest. Dichloro(ethylenediamine-N,N′-diacetato)platinum(IV) can exist in three possible isomers. One isomer has the two coordinated chloride groups *trans* to each other. The second isomer has one chloride group *cis* to the other but the two carboxyl groups *trans* to each other. In the third isomer the chloride groups are *cis* to each other as are the carboxyl groups.







When a square-planar platinum(II) compound is oxidized to an octahedral platinum(IV), it has been found in the past that the two incoming groups always go *trans* to each other,[2,3] which fact would make the two *cis*-dichloro isomers difficult to obtain through oxidation. The stereochemistry of the oxidation of platinum(II) complexes of ethylenediamine-N,N′-diacetic acid has been examined and it has been found that oxidation can give a *cis*-dichloro isomer. It has also been found

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[1] S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 6228 (1952).

[2] F. Basolo, J. C. Bailar, and B. R. Tarr, *ibid.*, **72**, 2433 (1950).

[3] A. Werner, "Lehrbuch der Stereochemie," 1904.