tion, then ether, and finally dried under an infrared lamp. It was reduced easily by alcohol or by iodide ion, the brown cobalt(II) complex salt being regenerated.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Co](ClO_4)_3$: C, 28.1; H, 3.7; N, 7.3. Found: C, 28.9; H, 3.9; N, 7.1.

1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-nickel(II) Perchlorate.—A solution of the base VII (0.75 g.) in methanol (5 ml.) was added to a solution of nickel(II) acetate tetrahydrate (0.5 g.) in water (50 ml.), the mixture rapidly boiled and then immediately cooled and filtered. Ten per cent. sodium perchlorate solution was then added to the brownish-red filtrate. The pink, silky precipitate which separated was recrystallized from warm water to which additions of sodium perchlorate were made and obtained in paramagnetic red needles (magnetic moment, 2.99 Bohr magnetons).

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Ni](ClO_4)_2$: C, 35.1; H, 3.6; N, 9.1. Found: C, 35.3; H, 3.6; N, 9.2.

1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-copper(II) Perchlorate.—A solution of the base VII (0.7 g.) in methanol (8 ml.) was added to a solution of copper(II) sulfate pentahydrate (0.7 g.) in water (10 ml.). Addition of 10% aqueous sodium perchlorate solution to the resultant green solution precipitated a green oil which solidified on scratching. It was purified by two rapid recrystallizations from hot water and obtained in green needles. Prolonged heating with water causes hydrolysis of the Schiff base.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Cu](ClO_4)_2$: C, 34.8; H, 3.6; N, 9.0; Cu, 10.2. Found: C, 34.6; H, 3.7; N, 9.0; Cu, 10.4.

Acknowledgment.—The authors gratefully acknowledge the assistance of Miss B. Stevenson who carried out the C, H and N microanalyses.

SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

A Four-coördinated Copper(II) Complex with a Tetrahedral Disposition of the Copper Valences

BY FRANCIS LIONS AND KENNETH V. MARTIN[1]

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The 4-coördinated copper(II) complexes of *dl*-, *d*- and *l*-2,2′-bis-(salicylideneamino)-6,6′-dimethyldiphenyl and of 2,2′-bis-(salicylideneamino)-diphenyl have been prepared. In them the four copper covalences must be tetrahedrally disposed.

With the single exception of cesium chlorocuprate, Cs_2CuCl_4, all X-ray analyses so far carried out of 4-covalent copper(II) complexes have shown them to have a square planar arrangement of the donor atoms about the metal atom. Helmholz and Kruh[2] considered from their studies of cesium chlorocuprate that in the crystal the complex ion was in the form of a tetrahedron distorted by flattening. On the other hand, spectral analysis showed that in solution the structure of the aquated ion is probably not the same as in the crystal and the tetrahedral configuration may be due to the exigencies of crystal packing.

Mills and Gott[3] claimed the preparation of a tetrahedral copper(II) complex in 1926—the copper derivative of benzoylpyruvic acid. However, many chemists have found it difficult to concede this claim.

Pauling,[4] on the basis of the X-ray results, proposed that the bonding orbitals used by copper in these 4-covalent complexes were $3d4s4p^2$, the unpaired electron being promoted to an outer 4p orbital. Such a promoted electron should be easily removed by oxidation and this behavior is not observed. Further, electronegative donor atoms are more likely to bond with 4d than with 3d orbitals. At the present time many chemists consider that 4-covalent copper(II) complexes involve the use of $4s4p^24d$ orbitals. This accounts satisfactorily for their stability to oxidation, their square planar arrangement, and the rapid interchange in solution of their donor molecules, behavior characteristic of upper level covalent bonds.

It seems surprising that tetrahedral 4-covalent copper(II) complexes do not seem so far to have been observed because the $4s4p^3$ bonding required for the tetrahedral arrangement is energetically feasible. There is some evidence which can be interpreted as showing that the spatial arrangement of organic chelate molecules about a central copper(II) atom can compel a tetrahedral arrangement of the four donor atoms. Thus Porter[5] has shown that 3,3′,5,5′-tetramethyl-4,4′-dicarbethoxy-dipyrrylmethene (I) functions as a bidentate chelate compound with many metals, coördinating with loss of a proton. In the copper(II) complex (II), first prepared by Schubert and Fischer,[6] the methyl groups in the 5- or 5′-positions of the dipyrrylmethene residues would clash very seriously in any attempt at a planar arrangement of this complex and Porter concluded that its configuration was non-planar and probably tetrahedral.

It occurred to us to design a quadridentate chelate compound with a molecule capable of presenting four donor atoms to a copper atom from the apices of a circumscribing tetrahedron but being incapable of functioning as a quadridentate in any other way. The first substance to be chosen was 2,2′-bis-(salicylideneamino)-6,6′-dimethyldiphenyl (III). Meisenheimer and Horing[7] have shown that the parent base 2,2′-diamino-6,6′-dimethyldiphenyl (IV) can be resolved into enantiomers and Kistiakowsky and Smith[8] have shown that these can be racemized only at relatively high temperatures and with difficulty. There is thus no possibility of the two benzene rings of the diphenyl system of IV or III being at any time coplanar under

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(2) L. Helmholz and R. F. Kruh, THIS JOURNAL, **74**, 1176 (1952).

(3) W. H. Mills and R. A. Gott, *J. Chem. Soc.*, 3121 (1926).

(4) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 104.

(5) C. R. Porter, *J. Chem. Soc.*, 368 (1938).

(6) M. Schubert and H. Fischer, *Ber.*, **57**, 611 (1924).

(7) J. Meisenheimer and M. Horing, *ibid.*, **60**, 1425 (1927).

(8) G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 1043 (1936).

ordinary conditions. Since atoms attached to a benzene ring lie in the plane of that ring, coördination of both the nitrogen atoms of IV, or a derivative of it such as III, to a metal atom, would require the metal atom to be held in such a position that it does not lie in either of the planes containing a benzene ring of the diphenyl system.

A model (see Fig. 1) shows that the two oxygen atoms and the two nitrogen atoms of III can be brought strainlessly into a tetrahedral arrangement from which they can all become attached to a central metal atom of appropriate size. Moreover, they cannot be disposed about the metal atom in a square planar arrangement or even a distorted square planar arrangement.

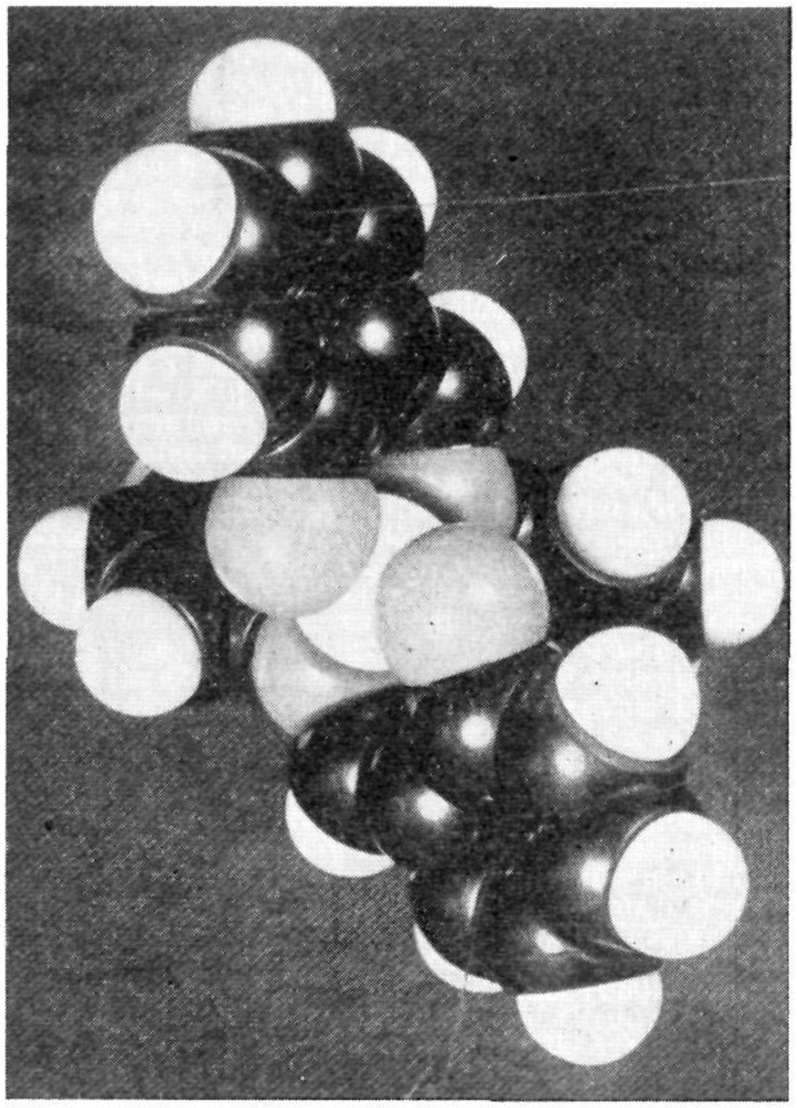
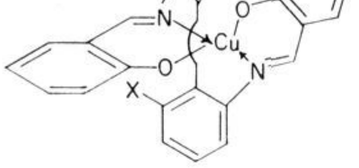


Fig. 1.



V, X = CH_3 VI, X = H

Treatment of *dl*-III with copper(II) acetate monohydrate in boiling methanol–ethyl acetate solution led to formation of *dl*-2,2′-bis-(salicylideneamino)-6,6′-dimethyldiphenyl-copper(II) (V), a greenish-brown crystalline substance which could be isolated with the help of chloroform and water. It was moderately soluble in organic solvents, and its molecular weight was determined to be 470 (average) instead of the calculated 482. It was paramagnetic with an observed magnetic moment of 1.95 Bohr magnetons.

The optically active forms of IV were obtained by the method of Meisenheimer and Horing[7] and the later modification of Dethloff and Mix[9] and converted into the optically active forms of III, from which were obtained the optically active forms of V. For monochromatic light the observed rotations of these *d*- and *l*-copper(II) complexes were of equal magnitude but opposite sign. It was interesting to note that the rotation of either optically active form changed sign in the region between 5461 Å. (mercury green line) and 5893 Å. (sodium D line). Maximum transmission of these complexes occurs at 5740 Å. The inversion of rotation may therefore be ascribed to a Cotton effect. However, this observation varies from those previously recorded in that whereas they usually occur in asymmetric metal complexes with additional centers of asymmetry in the organic chelate residues, in the copper(II) complex under discussion there is no such arrangement. It is, of course, true that the total molecular dissymmetry here may be thought of as due partially to dissymmetry due to the diphenyl system and partially to dissymmetry about the copper atom.

Support for the view that the copper covalences are tetrahedrally disposed in V is to be found in the ready preparation of a similar beryllium(II) complex from III—a golden-yellow crystalline solid typical non-valent complex. It has been thoroughly established that 4-covalent beryllium(II) has a tetrahedral disposition of its valences.[3]

It was not found possible, despite repeated attempts, to prepare an analytically pure nickel(II) complex. Craig and Mellor[10] have pointed out that almost all the 4-covalent nickel(II) complexes so far reported in which the donor atoms are two nitrogen atoms and two oxygen atoms have a planar distribution of the metal atom valences. Since the planar arrangement cannot be attained, III is apparently unable to coördinate normally with nickel(II).

Finally, it should be commented that valuable confirmatory evidence would be afforded by the preparation of a resolvable copper(II) complex from a symmetrical quadridentate similar to III. Thus, the unresolvable 2,2′-bis-(salicylideneamino)-diphenyl forms a copper(II) complex (2,2′-bis-(salicylideneamino)-diphenyl-copper(II) (VI)) very similarly constituted to V and which must exist in enantiomorphous forms. Resolution of VI by some such method as partial absorption on optically active quartz, or preparation of VI from an optically active copper(II) salt by the method of asymmetric induction would afford valuable subsidiary evidence, and it is hoped to report on such experiments soon.

Experimental

***dl*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl (III).**—The rather drastic conditions employed by Carlin

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[9] W. Dethloff and H. Mix, *Ber.*, **82**, 534 (1949).

[10] D. P. Craig and D. P. Mellor, *J. Proc. Roy. Soc., N.S.W.*, **74**, 475 (1940).

and Foltz[11] for the preparation of III are unnecessary. Salicylaldehyde (7 g.) was added to a boiling solution of IV (6.0 g.) in ethanol (30 ml.). The bright yellow bis-salicylal derivative soon crystallized out, and after 10 minutes was collected, recrystallized from ethanol, and thus obtained in yellow needles, m.p. 230°. Carlin and Foltz give the m.p. as 234–235°.

Anal. Calcd. for $C_{28}H_{24}N_2O_2$: C, 80.0; H, 5.7. Found: C, 79.7; H, 5.8.

dl-**2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl-copper(II)** (V).—A solution of copper(II) acetate monohydrate (0.5 g.) in methanol (40 ml.) was added to a boiling solution of III (1 g.) in ethyl acetate (15 ml.). The solution became deep olive-brown in color. Chloroform (100 ml.) was added. Then methanol and water-soluble salts were washed out by several treatments with water. Eventually the chloroform solution was dried (anhydrous sodium sulfate) and the solvent removed. The residual green-brown solid was recrystallized from ethanol and obtained in green-brown needles, m.p. 303°, moderately soluble in ethanol, benzene, ethyl acetate or acetone but insoluble in petroleum ether, methanol or water.

Anal. Calcd. for $C_{28}H_{22}N_2O_2Cu$: C, 69.7; H, 4.6; N, 5.8; Cu, 13.2; mol. wt., 482. Found: C, 69.2; H, 4.9; N, 5.4; Cu, 12.9; mol. wt. (Rast in camphor), 450–490.

This copper(II) complex was found to be paramagnetic with a magnetic moment of 1.95 Bohr magnetons.

l-**2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl.**—The *dl*-base IV was resolved with the help of *d*-tartaric acid according to the method of Meisenheimer and Horing.[7] The pure *l*-base formed colorless plates, m.p. 155–156° (from ethanol) with $[M]^{20}_{\mathrm{D}}$ −73.8° (in 0.3 *N* hydrochloric acid solution). Meisenheimer and Horing give m.p. 156° and $[M]^{20}_{\mathrm{D}}$ −74°. An ethanol solution of the pure *l*-base (0.6 g.) and salicylaldehyde (0.7 g.) was boiled for 5 minutes. After several recrystallizations from ethanol, the yellow solid Schiff base was obtained in needles m.p. 164°.

Anal. Found: C, 80.0; H, 5.8.

The specific rotation in ethyl acetate solution was $[\alpha]^{24}_{\mathrm{D}}$ −593° and $[\alpha]^{24}_{5461}$ −830°, equivalent to $[M]^{24}_{\mathrm{D}}$ −2490° and $[M]^{24}_{5461}$ −3445°.

l-**2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl-copper(II)** was prepared similarly to the *dl*-complex. It crystallized from benzene–petroleum ether in brown needles, m.p. 274°.

Anal. Found: C, 69.2; H, 4.9; N, 5.6; Cu, 13.0.

The specific rotation in ethanol $[\alpha]^{24}_{\mathrm{D}}$ was +75°, $[\alpha]^{24}_{5461}$ −100°, whence $[M]^{24}_{\mathrm{D}}$ +3600° and $[M]^{24}_{5461}$ −4800°.

d-**2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl.**—Dextrorotatory 2,2′-diamino-6,6′-dimethyldiphenyl, m.p. 157°, was prepared according to Dethloff and Mix.[9] Its solution in 0.3 *N* hydrochloric acid gave $[M]^{20}_{\mathrm{D}}$ +73.8°. The bis-salicylidene derivative formed yellow needles, m.p. 165°. A 50–50 mixture of the *d*- and *l*-Schiff bases had m.p. 228°.

Anal. Found: C, 79.8; H, 5.8.

The specific rotation in ethyl acetate solution was $[\alpha]^{24}_{\mathrm{D}}$ +582° and $[\alpha]^{24}_{5461}$ + 830° whence $[M]^{24}_{\mathrm{D}}$ +2445° and $[M]^{24}_{5461}$ +3445°.

d-**2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl-copper(II)** crystallized from benzene–petroleum ether in brown needles, m.p. 274°.

Anal. Found: C, 69.4; H, 4.7; N, 5.6; Cu, 12.9.

The specific rotation (ethanol) was $[\alpha]^{24}_{\mathrm{D}}$ −75° and $[\alpha]^{24}_{5461}$ +100°, whence $[M]^{24}_{\mathrm{D}}$ −3600° and $[M]^{24}_{5461}$ +4800°.

2,2′-Bis-(salicylideneamino)-diphenyl-copper(II).—A solution of salicylaldehyde (1.3 g.) and 2,2′-diaminodiphenyl (1 g.) in ethanol (10 ml.) was gently boiled for 5 minutes. After recrystallization the orange Schiff base formed prisms, m.p. 154°.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: C, 79.6; H, 5.1. Found: C, 79.4; H, 5.2.

A hot solution of copper(II) acetate monohydrate (1 g.) in methanol (40 ml.) was added to a hot solution of this Schiff base (0.5 g.) in ethyl acetate (20 ml.). The solution became deep olive green. On cooling, the copper(II) complex crystallized. Recrystallized from ethanol, it was obtained in olive needles, m.p. 301°.

Anal. Calcd. for $C_{26}H_{18}N_2O_2Cu$: C, 68.8; H, 4.0; Cu, 14.0. Found: C, 68.4; H, 4.0; Cu, 13.8.

This complex was paramagnetic with a magnetic moment of 1.95 Bohr magnetons at 22°.

dl-**2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl-beryllium(II).**—Basic beryllium acetate (2 g.) and III (1 g.) were heated together in chloroform (50 ml.) solution under reflux for 2 hours. The chloroform was then distilled off and the residue recrystallized many times from ethanol. It eventually was obtained in golden micro-needles, m.p. 289°.

Anal. Calcd. for $C_{28}H_{22}N_2O_2Be$: C, 78.7; H, 5.2; N, 6.5; Be, 2.1. Found: C, 78.9; H, 5.5.; N, 6.2; Be, 1.9.

Acknowledgment.—The authors gratefully acknowledge their indebtedness to Miss B. Stevenson for the C, H and N microanalyses recorded in this paper.

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(11) R. B. Carlin and G. E. Foltz, THIS JOURNAL, **78**, 200 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Olefin Coördination Compounds. II. The Preparation and Infrared Spectral Properties of Olefin–Platinum(II) Chloride Complexes[1,2]

BY HANS B. JONASSEN AND JACK E. FIELD

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The complex compounds $[PtCl_2{\cdot}C_4H_8]_2$, $[PtCl_2{\cdot}i\text{-}C_4H_8]_2$ and $[PtCl_2(C_4H_8)_2]$ have been prepared. The infrared spectra of 1,3-bis-(ethylene)-2,4-dichloro-μ-dichloroplatinum(II), 1,3-bis-(butene-1)-2,4-dichloro-μ-dichloroplatinum(II) and 1,3-bis-(isobutene)-2,4-dichloro-μ-dichloroplatinum(II) have been measured from 2 to 15 μ by the KBr disc method. Shifts in the $C{=}C$ frequencies indicate a carbon-to-carbon bond order of one and two-thirds for the complexes.

Introduction

Platinum (II) complexes containing an olefin as a ligand have been known since 1827 when Zeise first prepared and characterized potassium ethylenetrichloroplatinum(II).[3] Since then, a large number of olefin complexes with platinum have been prepared,[4] but the nature of the platinum–olefin bond has remained somewhat of a mystery. The most recent suggestion by Chatt[5] involves an

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(1) Abstracted in part from M.S. Thesis of J. E. Field, Tulane University, June, 1955.

(2) Presented at the American Chemical Society Meeting, Dallas, April, 1956.

(3) W. C. Zeise, *Pogg. Ann.*, **9**, 623 (1827).

(4) J. Chatt, *Ann. Rpts.*, **43**, 120 (1946).

(5) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).