ties. The generality of this reaction is further illustrated by treating bis(acetylacetonato)copper(II) in boiling benzene solution with 1-(2-pyridyl)3-(1-isoquinolyl)1,2-diaza-2-propene.[4] The resulting compound VId was distinguished by its intense reddish purple color in solution.

Structure of the Complexes.—Without complete X-ray structural analysis, it is not possible to assign unequivocal structures to the copper complexes described in this paper. The usual stereochemistry of copper(II) complexes is a square-planar arrangement of four donor atoms at normal bond distances around the metal ion with one or two more elongated bonds normal to the plane. The X-ray structural analysis of a five-coordinate zinc(II) complex has been reported[7]; it shows a tridentate ligand (terpyridine) and two halogen atoms all bonded to zinc in a trigonal-bipyramidal arrangement. The corresponding copper(II) complex was shown to be isomorphous with the zinc compound and therefore likely to have the same structure. More recently, the X-ray structural analysis of bis(bipyridine)copper(II) iodide was reported,[8] showing the copper to have a trigonal-bipyramidal configuration.

The conductivity data of the complexes III, IV, and V indicate a square-planar structure for these. In the complexes of type II, the tridentate PAPHY and two anionic ligands (halide or thiocyanate) appear to be bonded to the copper atom; the complexes are nonelectrolytes in nonpolar solvents. By analogy,[7,8] these are assigned a trigonal-bipyramidal structure.

The complexes of type VI are also assigned a trigonal-bipyramidal stereochemistry. The highly crystalline nature of some of these shows that they are not chance equimolecular mixtures of bis(PAPY)copper(II)[4] and the bis(β-diketone)copper(II) complexes. The infrared spectra (Table II) of these compounds show the presence of a deprotonated molecule of I and a β-diketone residue both bonded to the copper atom. The C=O and C=C stretching vibrations are assigned to bands at somewhat higher frequencies than those in bisacetylacetonatocopper(II). A tetragonal pyramidal structure is also possible for these complexes.

Acknowledgments.—The authors gratefully acknowledge the grant (919-Al) from the Petroleum Research Fund of the American Chemical Society which has made this work possible and the assistance of Miss B. Stevenson for all the organic microanalyses and spectra recorded.

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[7] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

[8] G. A. Barclay and C. H. L. Kennard, *Nature*, **192**, 425 (1961).

Notes

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3,5,6-Tri(2-pyridyl)1,2,4-triazine, a New Tridentate Chelating Agent, and Some of Its Metal Coordination Complexes

BY JOHN F. GELDARD[1]

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Multidentate chelating agents in which the donor atoms are sp^2-hybridized nitrogen atoms are usually of the strong ligand field type. Ligands such as terpyridine [2,6-di(2-pyridyl)pyridine], bipyridine, or 1,10-phenanthroline all cause spin pairing in the derived octahedral iron(II) complexes but not in the cobalt(II) and manganese(II) complexes. The donor nitrogen atom may be located in pyridine or other heterocyclic rings or in azomethine linkages such as hydrazones[2] or Schiff bases.[3]

Tridentate chelating agents of suitable low symmetry having such donor nitrogen atoms are interesting because they can make possible the study of some stereochemical problems associated with octahedral coordination.

In this paper the preparation of a new tridentate chelating agent, 3,5,6-tri(2-pyridyl)1,2,4-triazine (I), is described. The spectra, stereochemistry, and physical properties of its coordination complexes with some transition metal salts are discussed.

Experimental

Conductivities.—All electrical conductivities were measured with a Philips Philoscope and platinum coated electrodes of the dip-type. Values are given in ohm.$^{-1}$ cm.^{2} at 25° for about 10^{-3} *M* solutions in purified nitrobenzene and water.

Magnetic Moments.—Magnetic moments were measured on a Gouy balance at room temperature.

Electronic Absorption Spectra.—Spectra were measured in 95% ethanol using a Perkin-Elmer Model 4000A spectrophotometer.

1,2,5-Tri(2-pyridyl)5-amino-3,4-diazapent-2,4-dien-1-one (II).—A cold solution of 2-picolinicamidrazone[4a] (10 g.) in N-methyl-2-pyrrolidone (60 ml.) was added slowly with stirring to a solution of 2,2′-pyridil[4b] (16 g.) in N-methyl-2-pyrrolidone (30 ml.) at 100°. A white solid separated out toward the end of the addition. The mixture was cooled and the product collected. It crystallized from pyridine in cream-colored needles, m.p. 188–189°; the yield was 21 g.

Anal. Calcd. for $C_{18}H_{14}N_6O$: C, 65.4; H, 4.3. Found: C, 65.5; H, 4.6.

3,5,6-Tri(2-pyridyl)1,2,4-triazine (I).—II (15 g.) was heated in boiling N,N-dimethylformamide (25 ml.) until a clear yellow solution was obtained. The solution was cooled and diluted with water. The yellow precipitate was collected and recrystallized from aqueous N,N-dimethylformamide, m.p. 186–187°. The yield was 13 g.

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[1] W. A. Noyes Laboratory, University of Illinois, Urbana, Ill.

[2] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

[3] F. Lions and K. V. Martin, *ibid.*, **79**, 2733 (1957).

[4] (a) W. J. van der Burg, *Rec. trav. chim.*, **74**, 257 (1955); (b) commercial product.

TABLE I

METAL COORDINATION COMPLEXES OF I[a]

Compound no.	Formula	M.p., °C.	Magnetic moment, B.M.	Conductivity, ohm.$^{-1}$ cm.^{2}		Calcd., %					Found, %				
				Nitrobenzene	Water	C	H	N	X	M	C	H	N	X	M
IVa	$[ZnC_{18}H_{12}N_6 \cdot Cl_2]$	253–265	. . .	0.4	253.6	48.2	2.7	18.7	15.8	14.6	48.5	3.0	18.2	15.2	15.0
IVb	$[CuC_{18}H_{12}N_6 \cdot Cl_2]$	219–220	1.9	0.8	303.5	48.4	2.7	18.8	15.9	14.2	48.4	3.5	17.2	15.3	13.4
IVc	$[CuC_{18}H_{12}N_6 \cdot Br_2]$	300	1.9	1.9	343.0	40.4	2.3	15.7	29.8	11.9	40.9	2.5	15.4	30.1	11.7
IIIa	$[FeC_{36}H_{24}N_{12}](ClO_4)_2$	254	. . .	50.9	308.0	b									
IIIb	$[CoC_{36}H_{24}N_{12}](ClO_4)_2 \cdot 2H_2O$	252–260	3.9	50.7	286.8	47.1	3.1	18.3	7.7	6.4	47.1	3.4	17.4	7.0	6.7
IIIc	$[NiC_{36}H_{24}N_{12}](ClO_4)_2 \cdot H_2O$	259–265	3.5	60.5	210.5	48.0	2.9	18.7	7.9	6.5	47.9	3.2	17.8	7.6	6.9
IIId	$[CuC_{36}H_{24}N_{12}](ClO_4)_2 \cdot H_2O$	215–220	2.2	51.1	313.2	47.8	2.9	18.6	7.8	7.0	48.1	3.2	18.1	8.5	7.4
IIIe	$[ZnC_{36}H_{24}N_{12}](ClO_4)_2 \cdot {}^1/_2H_2O$	300	. . .	54.5	288.0	48.2	2.8	18.7	7.9	7.3	48.0	3.5	18.3	7.8	7.3

[a] Names of complexes: IVa, dichloro[3,5,6-tri(2-pyridyl)1,2,4-triazine]zinc(II); IVb, dichloro[3,5,6-tri(2-pyridyl)1,2,4-triazine]-copper(II); IVc, dibromo[3,5,6-tri(2-pyridyl)1,2,4-triazine]copper(II); IIIa, bis[3,5,6-tri(2-pyridyl)1,2,4-triazine]iron(II) perchlorate; IIIb, bis[3,5,6-tri(2-pyridyl)1,2,4-triazine]cobalt(II) perchlorate–2-water; IIIc, bis[3,5,6-tri(2-pyridyl)1,2,4-triazine]nickel(II) perchlorate–1-water; IIId, bis[3,5,6-tri(2-pyridyl)1,2,4-triazine]copper(II) perchlorate–1-water; IIIe, bis[3,5,6-tri(2-pyridyl)1,2,4-triazine]zinc(II) perchlorate–$^1/_2$-water. [b] Calcd. for $Fe[C_{36}H_{24}N_{12}](ClO_4)_2$: C, 49.2; H, 2.7; N, 19.1; Cl, 8.1. Found: C, 50.6; H, 3.5; N, 19.2; Cl, 7.2. The slight trace of tris complex could not be removed by recrystallization.

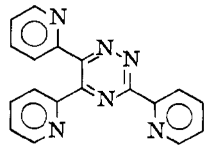
Anal. Calcd. for $C_{18}H_{12}N_6$: C, 69.2; H, 3.9. Found: C, 69.3; H, 3.8.

Coordination Complexes of Type IV.[5]—These compounds were prepared by heating the appropriate metal halide and I in equimolecular proportions in ethanol for 10 min., cooling, and collecting the product. IVa and IVb crystallized from aqueous ethanol and acetone, respectively. IVc was not recrystallized.

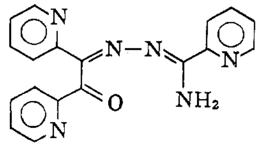
Coordination Complexes of Type III.[5]—The complexes were prepared by heating together the appropriate metal perchlorate–6-water (1 molecular proportion) and I (2 molecular proportions) in ethanol for 3 min. The solid that separated after cooling was collected and recrystallized from aqueous ethanol.

Discussion

The ligand I is readily obtained by the condensation of 2,2′-pyridil and 2-picolinicamidrazone in N-methyl-2-pyrrolidone solution and cyclization of the intermediate II. II can be cyclized by several methods, *e.g.*, boiling of ethanolic suspensions of II causes dissolution and simultaneous cyclization. Addition of acids to solutions of II causes immediate formation of I. The preparative method was the boiling of N,N-dimethylformamide solutions of II where yields of 91% were obtained.



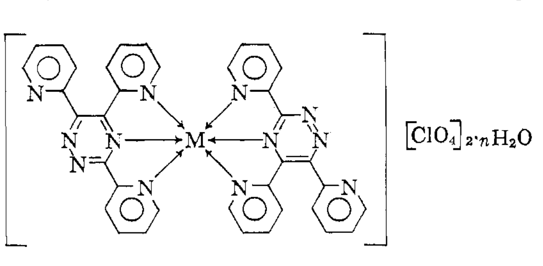
I



II

In complexes of I with six-coordinate metal ion, as in those of terpyridine, the ligand bonds to the metal ion through three equatorial apices of the coordination octahedron. Goodwin and Lions[6] have reported that 2,3,5,6-tetrakis(2-pyridyl)pyrazine functions only as a single tridentate chelate group; the pyrazine appears not to behave as a bifunctional ligand. Complexes of dimethylpyrazines have been reported,[7] however, in which two copper(I) ions or nickel(II) ions are bonded to the two nitrogen atoms. For the tetrakis(pyridyl)-pyrazine to function as a double tridentate chelating agent, all five rings must be coplanar. Such an arrangement, however, will cause steric interaction between the 3-hydrogen atoms of the adjacent pyridine rings. This steric interaction combined with the use of the very electronegative divalent transition metal ions is probably the reason for the observed single tridentate function of this ligand.

The ligand I showed no evidence that it could function as a bidentate and tridentate chelating agent simultaneously. There was some evidence that it could function singly as a bidentate group. It forms 2:1 complexes with Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) perchlorates (IIIa, b, c, d, and e, respectively). Magnetic moments and conductivity data (Table I) indicate that these are octahedral complexes in which I functions as a tridentate chelating agent. The elemental analyses of IIIa, however, indicate that some 3:1 complex with iron is formed and that here I behaves as a bidentate ligand. The stereochemistry of IIId is indeterminate; the magnetic moment and conductivity of the complex do not differentiate between an octahedral or square-planar structure. In



IIIa, M = Fe(II); $n = 0$
IIIb, M = Co(II); $n = 2$
IIIc, M = Ni(II); $n = 1$
IIId, M = Cu(II); $n = 1$
IIIe, M = Zn(II); $n = {}^1/_2$

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(5) The full names of these complexes and their physical properties and elemental analyses are given in Table I.

(6) F. Lions and H. Goodwin, *J. Am. Chem. Soc.*, **81**, 6415 (1959).

(7) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3156 (1963); *ibid.*, 5042 (1963).

TABLE II

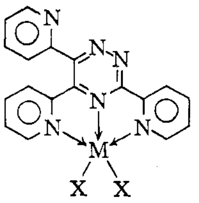
ELECTRONIC ABSORPTION SPECTRA OF I AND ITS COORDINATION COMPLEXES

Compound	λ_{max} (log ϵ)[a]				
I	244 (4.20)	284 (4.39)	382 (3.02)		
IIIa	242 (4.48)	285 (4.63)	380 (sh,[c] 4)	550 (3.65)	590 (sh, 3)
IIIb	. . .[b]	279 (4.62)	392 (3.96)		
IIIc	249 (4.42)	281 (4.54)	413 (3.85)		
IIId	. . .[b]	278 (4.63)	390 (3.98)		
IIIe	250 (sh, 4)	279 (4.58)	389 (3.89)		
IVa	. . .[b]	274 (4.22)	391 (3.79)		
IVb	. . .[b]	275 (4.36)	390 (3.90)		

[a] λ given in mμ, ε is the molar extinction coefficient. [b] Continuous absorption instead of a discernible peak was observed throughout this region. [c] Shoulder.

the latter structure, I would be a bidentate chelate group.

The ligand I can form 1:1 complexes with zinc(II) and copper(II) salts and the dichlorozinc(II), the dichlorocopper(II), and the dibromocopper(II) complexes (IVa, b, c, respectively) are described. Conductivity data indicate that these complexes probably have a trigonal-bipyramidal structure in their solutions in nitrobenzene.[8] The conductivity data also indicate that hydrolysis of these species to di-univalentel ectrolytes occurs in aqueous solution.



IVa, M = Zn(II); X = Cl
IVb, M = Cu(II); X = Cl
IVc, M = Cu(II); X = Br

The electronic absorption spectrum of I has peaks at [mμ (log ε)]: 244 (4.20), 284 (4.39), and 382 (3.02). These may be assigned to two π–π* transitions (244 and 284 mμ) and one n–π* transition (382 mμ). The absorption bands in the spectra of the complexes III and IV are principally due to the transitions of the ligand (Table II). Generally, the 244 and 382 mμ bands are shifted to longer wave lengths and the 284 mμ band to shorter wave lengths. In the iron(II) complex IIIa, all shifts are reversed. In addition, charge-transfer bands of the ferroin system are present at [mμ (log ε)] 550 (3.65) and 590 sh (3).[9]

The magnetic moments of IIIa and IIIb indicate that I is a strong-field ligand like terpyridine. Because I is of suitably lower symmetry than terpyridine, its octahedral complexes should exist in enantiomorphous forms. The optical activity of such complexes will be the subject of a future communication.

Acknowledgments.—The author acknowledges his indebtedness to Dr. F. Lions for having suggested the work to him and for helpful discussions and is grateful to Miss B. Stevenson for the organic microanalyses and the spectra recorded within.

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[8] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956); C. M. Harris, T. N. Lockyer, and H. Waterman, *Nature*, **192**, 424 (1961); G. A. Barclay and C. H. L. Kennard, *ibid.*, **192**, 425 (1961).

[9] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

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Substitution Pattern in Phenoxyphosphonitrilates

BY C. T. FORD, F. E. DICKSON, AND I. I. BEZMAN

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In the cyclic compound, hexachlorotriphosphonitrile, $(NPCl_2)_3$, progressive substitution of chlorine by other groups such as amino, aryl, or aryloxy can take place either geminally or around the ring. In two recent papers[1,2] we have demonstrated that proton magnetic resonance spectra can be used to determine both positional and *cis–trans* configurations of a series of dimethylaminotriphosphonitriles. We now report the extension of this procedure to delineation of the substitution pattern in the formation of phenoxy esters of $(NPCl_2)_3$ and present evidence that it is nongeminal.

Two reaction schemes were carried out as shown below.

$$(NPCl_2)_3 \xrightarrow[C_6H_6]{KOC_6H_5} \underset{\text{I}}{P_3N_3Cl_3(OC_6H_5)_3} \xrightarrow[THF]{HN(CH_3)_2(g)} \underset{\text{II}}{P_3N_3[N(CH_3)_2]_3(OC_6H_5)_3} \quad (1)$$

$$(NPCl_2)_3 \xrightarrow[(C_2H_5)_2O]{\text{aq. } HN(CH_3)_2} \underset{\text{III}}{P_3N_3[N(CH_3)_2]_3Cl_3} \xrightarrow[C_6H_5CH_3]{KOC_6H_5} \underset{\text{IV}}{P_3N_3[N(CH_3)_2]_3(OC_6H_5)_3} \quad (2)$$

In the first scheme, $(NPCl_2)_3$, C_6H_5OH, and KOH in a 1:4:4 mole ratio were refluxed in C_6H_6 for 2 hr., during which time the stoichiometric amount of H_2O required for formation of KOC_6H_5 was azeotroped out. Washing the product with dilute KOH and H_2O, drying, decolorizing, and removing solvent gave a water-white oil whose analysis indicated it to be compound I in 93% yield. Into a solution of the oil (I) in tetrahydrofuran at reflux was bubbled anhydrous dimethylamine, and a precipitate of $HN(CH_3)_2 \cdot HCl$ in stoichiometric quantity for complete replacement of the chlorine was formed in 6 hr. The residual solution was stripped of THF to give an oil which was dissolved in petroleum ether, decolorized, concentrated, and chilled to give a crystalline product, compound II, in 30% yield and melting at 90–92°.

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[1] I. I. Bezman and C. T. Ford, *Chem. Ind.* (London), 163 (1963).

[2] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).