Inorganica Chimica Acta, 25 (1977)L65–L66
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A New Bis-Chelating Ligand System. Synthesis and Chelating Behavior

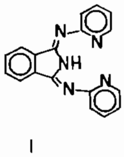
W. O. SIEGL

Engineering and Research Staff, Ford Motor Company, Dearborn, Michigan 48121, USA.

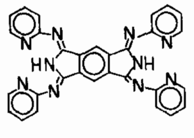
Received September 14, 1977

Of the few reported conjugated organic ligands capable of chelating more than one metal ion, those which exhibit a high degree of thermal stability usually exhibit low solubilities, thus severely limiting purification and investigations of solution chemistry [1–3]. Reported here is the synthesis of a series of substituted bis-chelating (dinucleating) ligands, and some representative bimetal chelate complexes, which incorporate high thermal stability and moderate solubility in organic solvents. The synthesis allows selected changes in certain properties (*e.g.* solubility) of the ligand by controlled modification of the molecular structure.

Each end of the new planar bis-chelating ligand is equivalent to a bis-1,3-(arylimino)isoindoline ligand [4, 5], 1 and accordingly may function as a uninegative tridentate ligand to occupy three co-planar sites of a square planar, trigonal bipyramidal, or octahedral coordination sphere [4, 6]. Due to the tridentate nature of the chelating ends of 2, the ligand represents a potential building block for the synthesis of a new class of conjugated polymetal-organometallics.



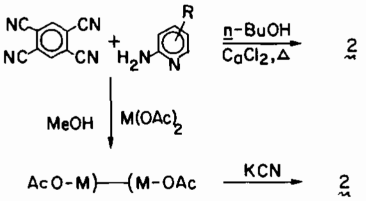
1



2

Synthesis and Characterization of the Ligand

The 1,3,5,7-tetra(2-pyridylimino)benzodipyrrole ligands 2 were obtained by two methods developed earlier for ligand 1 [5, 7]. Yields of purified ligands obtained *via* (eq. 1) are summarized in Table I. Products identical in all respects were obtained *via* (eq. 2).



(1)

(2)

The new ligands are high melting, yellow crystalline solids and except for **2d** and **2e**, which appear to be somewhat hygroscopic, have long shelf-lives. Parent ligand **2a** is very sparingly soluble, but the solubility is markedly increased by the introduction of alkyl groups in the 4-position of the pyridyl rings as shown in Table I. The ligands were characterized structurally by ir and nmr spectral data, elemental analyses, and coordination chemistry.

Synthesis and Characterization of Bimetal Complexes

To determine the chelating behavior of ligand 2 toward selected divalent transition metal ions, Job's Plots [8] were made for certain Cu(II) and Ni(II) salts. A new band appears in the visible spectrum at *ca.* 480 nm (presumably the M→L charge transfer) upon coordination of 2 with metal ions as shown in Fig. 1. Using the *ca.* 480 nm absorbance recorded 1–2 hr after mixing (DMF, 25 °C), Job's Plots for the complexation of 2c with $Cu(OAc)_2$, $Ni(OAc)_2$, and $NiCl_2$ exhibited maxima corresponding to metal:ligand stoichiometries of 2:1,

TABLE I. New Bis-Chelating Ligands: Yield and Solubility Data.

Compound No.	Ligand Derived from:	Mpt. °C	Yield	Solubility[a]
2a	2-aminopyridine	324–6	90	1.64
2b	2-amino-4-methylpyridine	340–1	59	0.64
2c	2-amino-4-ethylpyridine	353–5	45	46
2d	2-amino-4-propylpyridine	357–9	58	33
2e	2-amino-4-t-butylpyridine	435–7	44	1.1
2f	2-amino-4-s-butylpyridine	369–71	83	67
2g	2-amino-4-n-amylpyridine	317–8	49	7.3

[a] Solubility × 10^4 *M* in benzene at 23 °C.

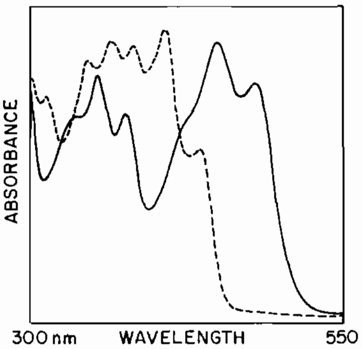


Fig. 1. Electronic spectra of bis-chelating ligand **2c** (- - - - -), and of its copper(II) acetate complex CuL'Cu (——) in DMF at 3.5 × 10^{-5} *M*.

2:1 and 1:1 respectively. The ratios are consistent with bimetal complex formation (eq. 3) in the first two cases and with metal–ligand polymer formation (eq. 4) with $NiCl_2$. The alternate explanation for the 1:1 stoichiometry, *i.e.*, formation of a monomeric 1:1 complex, appears unlikely because the optical density observed (478 nm) for a 1:1 mixture of $NiCl_2$ and ligand **2c** is consistent with the optical density calculated for the case where all the ligand ends are chelated, and is approximately double the value calculated for half of the ends uncomplexed. It should also be noted that monochelating ligand **1** readily forms NiL_2 with $NiCl_2$ under similar conditions.

$$2MX_2 + \underset{\mathbf{2}}{)\!-\!(} \longrightarrow \underset{\mathbf{3}}{X-M)\!-\!(M-X} + 2HX \qquad (3)$$

$$MX_2 + \underset{\mathbf{2}}{)\!-\!(} \longrightarrow X-[M)\!-\!(]_nM)\!-\!(\qquad (4)$$

Treatment of bis-chelating ligand **2f** with an excess of $Cu(OAc)_2$, $Ni(OAc)_2$, or $Pd(NCC_6H_5)_2Cl_2$ on a preparative scale allowed the isolation of the corresponding bimetal chelate complexes, **3**, in high yield according to (eq. 3). The bimetal complexes are high melting, air- and heat-stable, highly colored crystalline solids. As with the parent ligands, the solubilities of the bimetal complexes in organic solvents are very much dependent upon (alkyl) substituents on the periphery of the ligand; introduction of s-butyl groups increases the solubility of the CuL'Cu complex in benzene by more than two orders of magnitude to 1.4 × 10^{-4} *M*. Spectral and analytical data for the CuL'Cu, NiL'Ni and PdL'Pd complexes were consistent with structure **3**.

A unique feature of bis-chelating ligand **2** is that each chelating end is only tridentate, thus the ends of two different ligand molecules may coordinate to the same octahedral metal center. Therefore, with equimolar amounts of **2** and $NiCl_2$ a metal–ligand polymer might be expected (re: Job's plot). As a model for such chemistry (eq. 4) an attempt was made to cap the metal ions of the NiL'Ni complex **4** with mono-chelating ligand **1** to prepare what might be considered a molecular dumbbell with a Ni(II) ion embedded in the organic sphere at each end.

Treatment of complex **4** with two equivalents of mono-chelating ligand **1** in a non-coordinating solvent ($CHCl_3$, 25 °C) yielded a new highly soluble, rust color crystalline solid which exhibited spectra (ir, visible) and analytical data consistent with structure **5** as expected from (eq. 5);

$$\underset{\mathbf{4}}{AcO-Ni)\!-\!(Ni-OAc} + 2\ \underset{\mathbf{1}}{(} \longrightarrow \underset{\mathbf{5}}{(Ni)\!-\!(Ni)} + 2HOAc \qquad (5)$$

$$\underset{\mathbf{2f}}{)\!-\!(} + 2\ \underset{\mathbf{6}}{(Ni-OAc} \longrightarrow \mathbf{5} + 2HOAc \qquad (6)$$

the molecular weight (by osmometry) was 1699 (calcd 1680). The structure of complex **5** received additional support by its independent synthesis from free bis-chelating ligand **2f** and the nickel acetate complex **6** of the mono-chelating ligand **1** (eq. 6). The materials obtained from (eq. 5) and (eq. 6) were spectroscopically identical.

The reactions of these new bis-chelating ligands to form mixed-metal complexes and to form organometallic polymers are under investigation as are various physical and chemical properties of the new complexes.

Acknowledgment

The author thanks Dr. L. R. Mahoney for encouragement and helpful suggestions, and F. C. Ferris and P. A. M. Mucci for technical assistance.

References

1 U. T. Mueller-Westerhoff, *Advances in Chemistry Series, 150*, "Inorganic Compounds with Unusual Properties", R. B. King, Ed., American Chemical Society, Washington, D.C. (1976) p. 31.
2 P. H. Merrell and R. A. Osgood, *Inorg. Chim. Acta, 14*, L33 (1975).
3 F. B. Fleisher, L. Sklar, A. Kendall-Torry, P. A. Tasker and F. B. Taylor, *Inorg. Nucl. Chem. Letters, 9*, 1061 (1973).
4 J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5000 (1952); P. F. Clark, J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 3593 (1953).
5 W. O. Siegl, *J. Org. Chem., 42*, 1872 (1977).
6 W. O. Siegl, *J. Organometal. Chem., 107*, C27 (1976).
7 W. O. Siegl, *Inorg. Nucl. Chem. Letters, 10*, 825 (1974).
8 M. M. Jones, "Elementary Coordination Chemistry", Prentice-Hall, Englewood Cliffs, N.J. (1964) p. 282.