

Synthesis of Macrocyclic Nickel(II) Complexes containing the 2,2'-Bi-indolyl Moiety

David St C. Black,* Naresh Kumar, and Laurence C. H. Wong

School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, New South Wales, 2033, Australia

An effective synthesis of a 7,7'-diformyl-2,2'-bi-indolyl has been developed; this compound can undergo metal template macrocyclization reactions with suitable diamines and nickel(II) acetate.

Macrocyclic metal complexes have been formed from a variety of dialdehydes containing one or two supporting donor atoms.¹⁻⁴ One such compound was a 2,7-diformylindole⁴ and we wished to investigate the chelation potential of a 7,7'-diformyl-2,2'-bi-indolyl. We thus required a 2,2'-bi-indolyl suitably activated to enable formylation occur at the 7- and 7'-positions and set out to synthesize compounds (1) and (2).

Acid-catalysed dimerization⁵ of 4,6-dimethoxy-3-methylindole⁴ yielded the indolyl-indoline (9) as its hydrochloride in 70% yield. However, compound (9) could only be converted by established methods⁶ into the bi-indolyl (1) in poor yield and consequently a more satisfactory route was developed.

N,N'-Carbonyl-bis-4,6-dimethoxyindole (10), obtained from the reaction of 4,6-dimethoxyindole⁷ and *N,N'*-carbonyldi-imidazole, underwent palladium(II) acetate catalysed oxidative coupling⁸ to give the bi-indolyl (12) in 65% yield. Reduction with excess of lithium aluminium hydride or hydrolysis with barium hydroxide converted (12) into 4,4',6,6'-tetramethoxy-2,2'-bi-indolyl (3) [m.p. 278–280 °C; 60% yield; *m/z* 352; ¹H n.m.r. δ 3.78 and 3.86, OMe; 6.17, d, *J* 2 Hz, H-5; 6.47, d, *J* 2 Hz, H-7; 6.74, d, *J* 2.2 Hz, H-3; 11.2, d, *J* 2.2 Hz, NH (exchangeable)]. Unfortunately, the related conversion of (11) into (13) could not be achieved, so a less direct route to (1) was necessary. Vilsmeier formylation of (3) with one equivalent of phosphoryl chloride gave the monoformyl compound (4) and with two equivalents gave the diformyl compound (5). Reduction of (4) with lithium

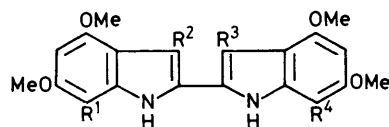
aluminium hydride in tetrahydrofuran yielded the rather reactive methyl compound (6) (70%, m.p. 189–190 °C).

Attempts to synthesize (6) directly⁹ from 4,6-dimethoxy-3-methylindole, 4,6-dimethoxyindolin-2-one, and phosphoryl chloride generated it under conditions which caused its rapid decomposition.

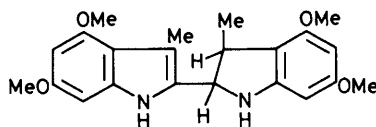
Formylation of (6) led to the more stable compounds (7) and (8) with one or two equivalents of reagent respectively. Reduction of (7) with excess of lithium aluminium hydride gave the target compound (1) [m.p. 113–115 °C; 60% yield; *m/z* 380; ¹H n.m.r. δ 2.30, Me; 3.75 and 3.82, OMe; 6.12, d, *J* 2 Hz, H-5; 6.41, d, *J* 2 Hz, H-7; 10.72, NH (exchangeable)]. Formylation of (1) gave (2) [80% yield; ¹H n.m.r. δ 2.61, Me; 3.88 and 3.94, OMe; 6.37, s, H-5; 10.7, CHO; 11.5, NH (exchangeable)].

Metal template reaction of (2) with 1,2-diaminoethane or 1,3-diaminopropane in the presence of nickel(II) acetate and triethylamine yielded the deep red complexes (14) and (15) respectively [e.g. (15) *m/z* 530 (100%, ⁵⁸Ni); ¹H n.m.r. δ 1.9 and 2.72, m, CH₂; 3.87 and 3.93, OMe; 5.89, s, H-5; 8.16, imine H].

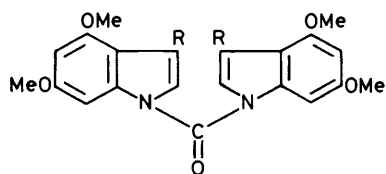
Attempts to prepare the related macrocyclic complexes from (2) and 1,2-diaminobenzene or 1,8-diaminonaphthalene were unsuccessful and led to the isolation of the nickel complex of dialdehyde (2) itself. The macrocyclization results are consistent with the geometry shown by a related pre-macrocyclic complex and described in the preceding communication.¹⁰



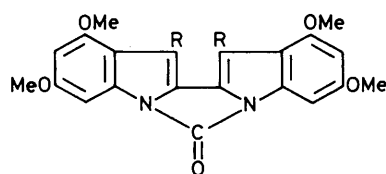
- (1) R¹ = R⁴ = H, R² = R³ = Me
- (2) R¹ = R⁴ = CHO, R² = R³ = Me
- (3) R¹ = R² = R³ = R⁴ = H
- (4) R¹ = R³ = R⁴ = H, R² = CHO
- (5) R¹ = R³ = H, R² = R⁴ = CHO
- (6) R¹ = R³ = R⁴ = H, R² = Me
- (7) R¹ = R⁴ = H, R² = Me, R³ = CHO
- (8) R¹ = R³ = CHO, R² = Me, R⁴ = H



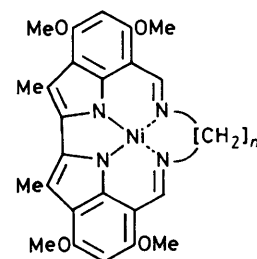
(9)



- (10) R = H
- (11) R = Me



- (12) R = H
- (13) R = Me



- (14) n = 2
- (15) n = 3

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References

- 1 D. St C. Black, C. H. Bos Vanderzalm, and A. J. Hartshorn, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 657; *Aust. J. Chem.*, 1982, **35**, 2435.
 - 2 D. St C. Black and N. E. Rothnie, *Aust. J. Chem.*, 1983, **36**, 2387.
 - 3 D. St C. Black and N. E. Rothnie, *Aust. J. Chem.*, 1983, **36**, 2395.
 - 4 D. St C. Black, and N. E. Rothnie, and L. C. H. Wong, *Tetrahedron Lett.*, 1980, **21**, 1883; *Aust. J. Chem.*, 1983, **36**, 2407.
 - 5 G. F. Smith and A. E. Walters, *J. Chem. Soc.*, 1961, 940.
 - 6 A. Z. Britten and G. F. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1972, 418.
 - 7 V. H. Brown, W. A. Skinner, and J. I. de Graw, *J. Heterocycl. Chem.*, 1969, **6**, 539.
 - 8 J. Bergman and N. Eklund, *Tetrahedron*, 1980, **36**, 1439.
 - 9 D. St C. Black and N. Kumar, *J. Chem. Soc., Chem. Commun.*, 1984, 441.
 - 10 D. St C. Black, D. C. Craig, N. Kumar, and L. C. H. Wong, *J. Chem. Soc., Chem. Commun.*, preceding communication.
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