

should also enable direct observation of the central atom in the case of $\{[(\text{Ph}_3\text{P})\text{Au}]_4\text{N}\}^+$.

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$[(\text{LAu})_6 \text{ } ^{13}\text{C}](\text{BF}_4)_2$, 137008-25-4; L, 739-58-2; LAuCl , 137008-26-5; $(\text{Me}_2\text{S})\text{-AuCl}$, 29892-37-3; $^{13}\text{C}\text{Cl}_4$, 32488-50-9; $\text{ClB}(\text{OMe})_2$, 868-81-5; $^{13}\text{C}[\text{B}(\text{OMe})_2]_4$, 137051-00-4.

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- [12] ^{13}C NMR (CD_2Cl_2): δ = 40.05 (s, CH_3), 112.25 (C3), 113.10 (C1, J = 65.6 Hz), 129.30 (C3'), 131.33 (C4'), 132.11 (C1', J = 55.8 Hz), 133.88 (C2'), 135.83 (C2), 152.55 (C4); ^1H NMR (CD_2Cl_2): δ = 2.78 (CH_3), 6.67 (H3), 6.92 (H2), 7.22–7.37 (m, residual H (arom.)).
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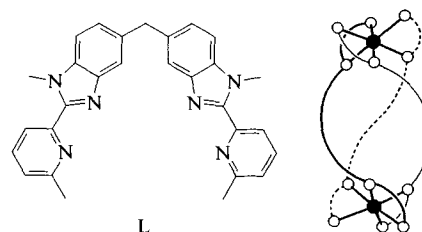
A Self-Assembling Triple-Helical Co_2^{II} Complex: Synthesis and Structure**

By Alan F. Williams,* Claude Piguet,
and Gérald Bernardinelli

A theme of considerable interest in supramolecular chemistry is the selective and spontaneous assembly of supermolecules by the complexation of polydentate ligands around two or more metal ions.^[1] Double-helical structures may be generated by two "oligobidentate" ligands complexing cations with a preference for tetrahedral coordination—

the metal–metal axis is the helical axis about which the ligands are twisted. Lehn et al.^[2] have synthesized a series of oligobipyridyl ligands which form double-helicates containing as many as five Cu^{I} ions, while Sauvage et al.^[3] have used the double-helical complex formed by Cu^{I} with a ligand containing two phenanthroline units linked by a $(\text{CH}_2)_4$ -bridge as a precursor for the synthesis of a molecular knot. Tetrahedral coordination of the metal is not an essential requirement for the formation of a helical structure, and we recently reported^[4] a double-helical complex of Cu^{I} in which the ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbz-impy) acts essentially as a bis(monodentate) ligand, giving a linear coordination of the two copper ions.

A basic requirement for self-assembly around metal ions is that the coordinating possibilities of the ligands should match the stereochemical preference of the metal ion. We may therefore predict for ions with a preference for octahedral coordination the possible formation of double-helical complexes from bis(terdentate) ligands and of triple helices from bis(bidentate) ligands. The first possibility has recently been shown to occur in the complex $[\text{Cd}_2(\text{sexipyridyl})_2]^{4+}$ reported by Constable.^[5] In this communication we report the crystal structure of a triple-helical complex which is formed on mixing stoichiometric amounts of the bis(bidentate) ligand bis[1-methyl-2-(6'-methyl-2'-pyridyl)benzimidazol-5-yl]methane (L) and cobalt(II) ions.



Scheme 1. Left: Structure of the ligand L. Right: Schematic representation of the helical complex formed from L and Co^{II} ions. Co atoms are shown as black spheres, N atoms as white spheres.

The ligand L has four coordination sites, but the rigidity of the aromatic rings prevents it from acting as a tetradentate ligand, and repulsion between the hydrogens in position 4 of the benzimidazoles destabilizes a planar structure. It is therefore ideally suited to act as a bis(bidentate) ligand. Reaction with cobalt(II) perchlorate leads to the isolation of orange salts with the composition $[\text{Co}_2\text{L}_3(\text{ClO}_4)_4]$; the rose-orange color of the crystals suggested a probable octahedral coordination of the cobalt, and the stoichiometry is in agreement with a triple-helical structure.

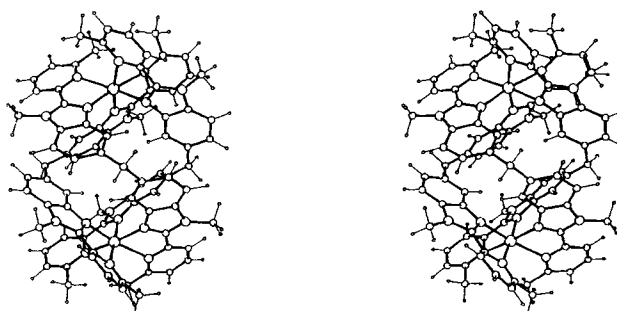


Fig. 1. Stereoview of the triple-helical cation $[\text{Co}_2\text{L}_3]^{4+}$ along one of the approximate C_2 axes.

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The X-ray crystal structure determination of $[\text{Co}_2\text{L}_3(\text{ClO}_4)_4 \cdot 2.5\text{CH}_3\text{CN}]$ confirms the existence of a triple-helical cation with approximate D_3 symmetry. Figure 1 shows an ORTEP^[6] stereoview of the cation along one of the C_2 axes which passes through one of the methylene carbon atoms and the midpoint between the two cobalt atoms. Figure 2 gives computer-generated representations of

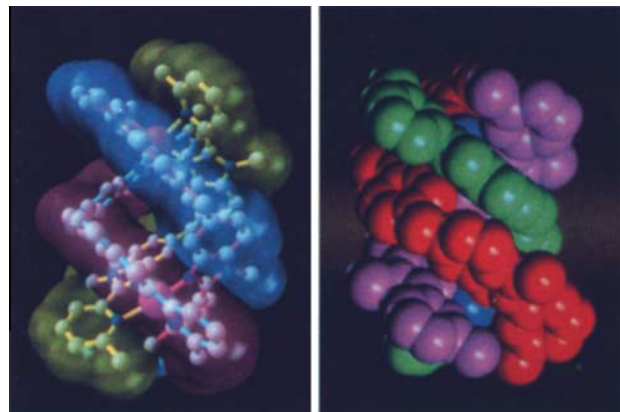


Fig. 2. Left: View [14] of the triple-helical cation $[\text{Co}_2\text{L}_3]^{4+}$ with the ligands represented by a ball-and-stick model surrounded by a translucent Connolly surface [15]. Right: View [16] of the triple-helical cation $[\text{Co}_2\text{L}_3]^{4+}$ with the non-hydrogen atoms represented as spheres with radii 80% of the van der Waals radius showing how the ligands wrap round the C_3 axis.

the structure in which the different strands are shown in different colors. Figure 3 shows a projection down the Co–Co axis. The perchlorate anions and the acetonitrile molecules have been omitted; one of the perchlorates showed five positions for the oxygens, but the other three were relatively well ordered. Five solvent molecules were found, but the sites were not totally occupied, and they were refined with a population parameter of 0.5.

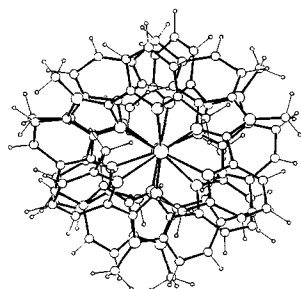


Fig. 3. View along the Co–Co axis showing the approximate C_3 symmetry.

The coordination sites of the two cobalt atoms are very similar, and in Table 1 we give the structural parameters obtained by averaging bond distances and angles related by pseudo D_3 symmetry. The cobalt coordination sphere may best be described as an octahedron flattened along a C_3 axis. The Co–N(benzimidazole) distance (2.07(2) Å) is shorter than the literature value of 2.103 Å^[7] for high spin octahedral cobalt(II), but the Co–N(pyridine) distance 2.29(6) Å is longer than the standard value of 2.185 Å. We attribute this distortion to repulsion between the methyl groups on posi-

tion 6 of the pyridine, since the distances between the carbon atoms of these methyls are quite short (average value 4.05(2) Å). This is supported by the observation that the average pyridine–Co–pyridine angle of 103° is significantly greater than the average benzimidazole–Co–benzimidazole angle (97°). The average ligand “bite angle” is 76.2°, and the cobalt–cobalt distance is 8.427(4) Å.

Table 1. Structural data for the cobalt coordination sphere, py = pyridine, bzim = benzimidazole.

	average [e.s.d.] [Å]	minimum	maximum
Co–N _{py}	2.29(6)	2.24	2.40
Co–N _{bzim}	2.07(2)	2.04	2.10
ligand “bite angle”	76(2)	74.0	78.4
py–Co–py	103(4)	96.9	106.9
bzim–Co–bzim	97(2)	95.2	99.5
bzim–Co–py	172(2)	171.0	174.4
bzim–Co–bzim	84(3)	79.7	89.2

[a] Bond lengths [Å] and angles [°] are averaged assuming D_3 symmetry, and the quoted e.s.d. are obtained from the six values used to obtain the average. The experimental e.s.d. are smaller.

The aromatic rings of the ligands are planar within experimental error, and the interplanar angles are given in Table 2. The average angle between the pyridine and the benzimidazole planes of a chelate ring is 22.7°, and between the two benzimidazole planes of one strand is 80°, but the spread of values is several degrees. Although the coordination sites of

Table 2. Interplane angles [°] between aromatic rings.

Ring [a]	pA1	bA1	bA2	pA2	pB1	bB1	bB2	pB2	pC1	bC1	bC2
bA1	24.0										
bA2	86.6	79.1									
pA2	82.7	87.7	30.5								
pB1	75.1	52.6	52.9	81.3							
bB1	85.6	67.2	32.1	62.3	22.6						
bB2	58.0	70.2	50.5	27.9	87.9	76.3					
pB2	33.2	49.3	66.3	51.7	84.1	81.9	25.0				
pC1	80.7	82.5	22.6	8.6	72.7	53.9	30.8	52.2			
bC1	69.0	76.3	37.0	14.0	81.0	65.7	14.7	37.7	16.1		
bC2	56.3	32.4	68.3	91.3	22.5	43.0	87.3	74.6	83.2	85.9	
pC2	70.1	47.4	54.8	82.0	5.1	26.1	86.1	80.5	73.5	80.45	17.7

[a] The rings are denoted as pyridine p or benzimidazole b, belonging to ligand strand A, B, or C, and bound to Co1 or Co2. Thus pB2 is the pyridine of strand B that is bound to Co2. The error in the angles is typically 1°.

the cobalt ions are approximately related by D_3 symmetry, the complex as a whole deviates significantly from this high symmetry (Fig. 3). This deviation is essentially due to the spread in torsion angles which are not expected to be strongly constrained, and suggest that the molecule is fairly flexible. In support of this we note the absence of the strong stacking interactions observed^[4] in $[\text{Cu}_2(\text{mbzimpy})_2]^{2+}$; in $[\text{Co}_2\text{L}_3]^{4+}$ there is evidence of some slight stacking between benzimidazoles in different strands, but the planes are not parallel, and the distances between the benzimidazoles, calculated using those atoms which show the greatest overlap, lie in the range 4.2 to 4.6 Å compared with the 3.4 Å observed previously.^[4] It therefore seems probable that the self

assembly is directed by the coordination requirements of the cation rather than by interligand interactions.

This is, to our knowledge, the first triple-helical coordination compound which has been characterized by X-ray crystallography. Libman, Tor, and Shanzer^[8] reported a triple-helical dinuclear iron complex which was characterized by ¹H NMR and CD spectra, but in this case the tripodal nature of the ligand undoubtedly plays an important role in structuring the complex. Another Fe₂ complex composed of two Fe^{II} centers with octahedral coordination and three bidentate ligands was reported recently,^[9] but in this case a triple-helical structure was not observed, presumably as a result of the greater flexibility of the ligands.

Experimental

The ligand L was obtained by a Phillips condensation of 3,3'-diamino-4,4'-bis(*N*-methylamino)diphenylmethane (prepared according to a modified literature procedure [10]) with 2-methylpyridine-6-carboxylic acid [11]. Crystals of [Co₂L₃(ClO₄)₄ · 2.5 CH₃CN] were grown from acetonitrile solution at 40 °C. A red-orange crystal (0.22 × 0.32 × 0.32 mm³) was sealed in a capillary tube with some of the supernatant liquid. *M*_r = 1994, triclinic *P* $\bar{1}$, *a* = 14.403(2), *b* = 16.558(3), *c* = 21.328(3) Å, α = 78.15(1)°, β = 81.19(1)°, γ = 89.02(1)° based on 24 reflections ($16^\circ < 2\theta < 31^\circ$), *V* = 4919(1) Å³, *Z* = 2. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with MoK α radiation (λ = 0.71069 Å), $4^\circ < 2\theta < 38^\circ$, 7877 unique reflections measured. Structure solved by direct methods [12], other calculations made using the XTAL system [13]. Full matrix refinement was performed successively on ligand 1 and cobalt, ligand 2, ligand 3 and perchlorate and solvent molecules (maximum of variables = 335). All atoms other than perchlorate oxygens and carbons of solvent molecules were refined with anisotropic thermal displacement parameters. Final *R* factor 11.0% (*R*_w = 9.7%, $w = 1/\sigma^2(F_o)$), for 4980 observed reflections ($|F_o| > 4\sigma(F_o)$). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge, CB2 1EW (UK), on quoting the full journal citation.

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L, 136629-58-8; [Co₂(L₃)](ClO₄)₄ · 2.5(CH₃CN), 136642-58-5; [Co₂L₃](ClO₄)₄, 136642-57-4; 3,3'-diamino-4,4'-bis(*N*-methylamino)diphenylmethane, 23816-42-4; 2-methylpyridine-6-carboxylic acid, 934-60-1.

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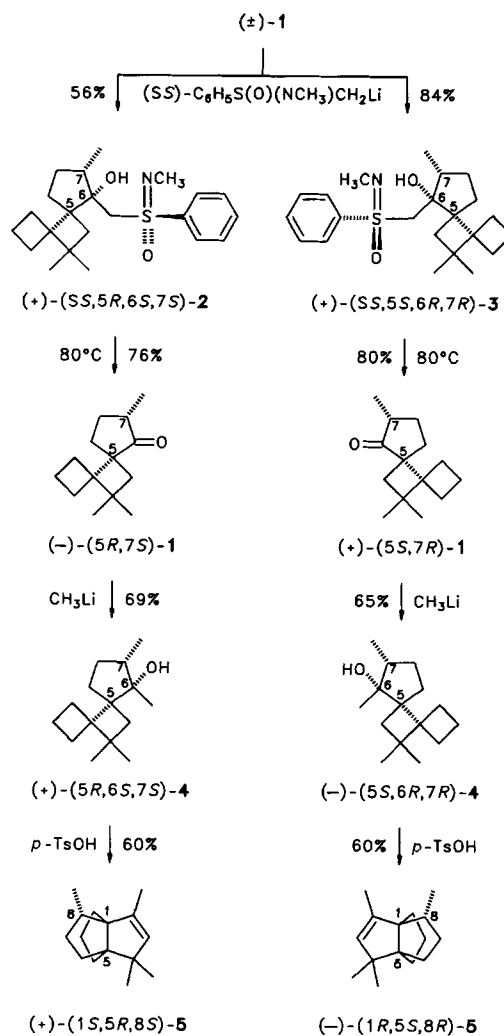
Synthesis, Absolute Configuration and Specific Rotation of (+)- and (–)-Modhephene**

By Lutz Fitjer,* Honorato Monzó Oltra, and Mathias Noltemeyer*

Dedicated to Professor Michael Hanack on the occasion of his 60th birthday

Since its discovery in *Isocoma wrightii*,^[1] a plant toxic to sheep and cattle in the south west USA, (–)-modhephene (5) has been a popular goal of synthetic studies. Because of a growth-inhibiting function of derivatives,^[2] related compounds have also been investigated. Twelve diastereoselective^[3] and one enantioselective syntheses^[4a–c] document an intense interest.

The only enantioselective synthesis^[4a–c] assigns (–)-modhephene a (1*R*,5*S*,8*R*) configuration on the basis of the circular dichroism of a cyclopropyl ketone precursor. The



Scheme 1. (+)- (1*S*,5*R*,8*S*)-5

(–)- (1*R*,5*S*,8*R*)-5

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