

Note

Mono- versus dinuclear cobalt complexes of a binucleating Schiff base ligand

S. Sandí-Ureña and E.J. Parsons*

Department of Chemistry, Clemson University, Clemson, SC 29634-1905 (USA)

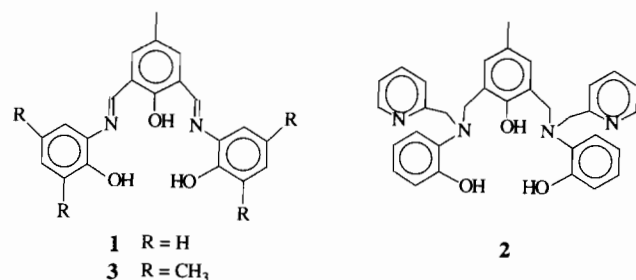
(Received April 3, 1993; revised June 28, 1993)

Abstract

The Schiff base ligand 2,6-bis[2-[(3,5-dimethyl-2-hydroxyphenyl)imino]-methyl]-4-methylphenol (H_3L), when reacted with $CoCl_2$ forms the monocobaltic complex, $HLCoCl$ (**5**). This diamagnetic complex is readily characterized by two-dimensional 1H NMR spectroscopy. Complex **5** reacts with a second cobalt ion in the presence of sodium benzoate to form $LCo^{II}Co^{III}(Cl)(O_2CC_6H_5)$. Comparisons are made between this complex and the dicobaltic complex of the analogous polypodal ligand 2,6-bis[[(2-hydroxyphenyl)(2-pyridylmethyl)amino]-methyl]-4-methylphenol.

Introduction

The bifunctional nature of dimetallic complexes makes them attractive candidates for the activation of small molecules. We have been developing complexes of binucleating macroligands of the Schiff base **1** [1, 2] and polypodal **2** [3] types specifically for this purpose. These ligands have similar frameworks, but the polypodal ligands occupy four sites per metal compared to three sites occupied by the planar Schiff base ligands. The complementary nature of these ligands makes comparison of their respective complexes desirable.



*Author to whom correspondence should be addressed.

We have recently reported diferric complexes of both **1** and **2** as well as a dicobaltic complex of **2** [3, 4]. In addition, Robson and co-workers have reported dicobaltous and mixed valent cobalt complexes of **1** [5, 6]. In order to better compare the full set of complexes, we synthesized an analog of Robson's complex based on the more soluble, tetramethylated ligand **3**, and attempted to oxidize it to the dicobaltic form. In the course of these reactions, we discovered that a minor modification to the synthesis of the dicobalt complex causes it to proceed via a stable monocobaltic complex. The synthesis and characterization of the monocobaltic complex is reported here, along with some relevant comparisons between the various dicobalt complexes.

Experimental

General

2-Hydroxy-5-methylisophthalaldehyde was synthesized by the method of Taniguchi [7]. 2,6-Bis[2-[(2-hydroxyphenyl)imino]methyl]-4-methylphenol and its methylated derivatives were synthesized by the method of Robson [1, 2]. Methanol and dimethylformamide (DMF) were dried prior to use and $CoCl_2 \cdot 2H_2O$ was prepared by heating $CoCl_2 \cdot 6H_2O$ at 110 °C for 30 min.

NMR spectra were obtained in pyridine- d_5 or methanol- d_4 at 25 °C on a Bruker AC300 spectrometer. Electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer in DMF solution. Cyclic voltammograms were determined in DMF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A PAR 273 potentiostat with platinum-disk working electrode, platinum-wire auxiliary electrode, and a SCE reference electrode were used. The ferrocenium/ferrocene couple was included as an internal standard. Energy dispersive X-ray spectra were obtained on a JEOL model IC 848. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Molecular weight was determined by Galbraith Laboratories, Knoxville, TN.

$HLCoCl$ (**4**)

A suspension of 140 mg 6-amino-2,4-dimethylphenol (1.02 mmol) and 85–170 mg $CoCl_2 \cdot 2H_2O$ (0.51–1.02 mmol) in 5.0 ml methanol was added to a warm solution of 5-methylisophthalaldehyde (0.51 mmol) in 5.0 ml methanol. The resulting solution was stirred just below its boiling point for 25 min. Formation of a red suspension occurred within 5 min. The mixture was then

filtered and the resulting red solid was washed with methanol and dried under vacuum at ambient temperature. An identical complex was obtained upon addition of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ to the pre-assembled ligand suspended in methanol. Yield 103 mg, 64%. *Anal.* Calc. for $\text{HLCoCl} \cdot 1.5\text{H}_2\text{O}$, $\text{C}_{25}\text{H}_{27}\text{ClCoN}_2\text{O}_4$: C, 57.54; H, 5.21; Cl 6.80. Found: C, 57.43; H, 5.26; Cl, 7.51%. FW Calc. for $\text{HLCoCl} \cdot 1.5\text{H}_2\text{O}$, 521.88 g mol⁻¹; FW Calc. for $[\text{HLCo}(\text{DMF})]\text{Cl} \cdot 1.5\text{H}_2\text{O}$, 594.98 g mol⁻¹ (297.49 g mol⁻¹). Found (DMF): 298 g mol⁻¹. UV (DMF) $\lambda_{\text{max}} = 488 \text{ nm}$ ($\epsilon = 14\,000 \text{ M}^{-1} \text{ cm}^{-1}$).

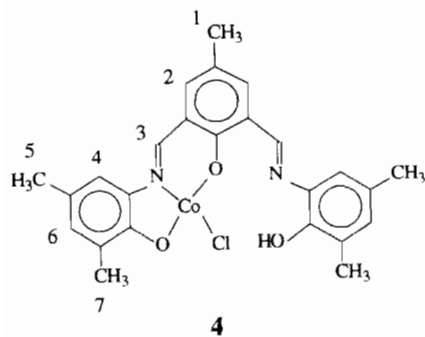
$\text{LCo}_2(\text{O}_2\text{CC}_6\text{H}_5)\text{Cl}$ (5)

The dicobalt complex $\text{LCo}_2(\text{O}_2\text{CC}_6\text{H}_5)\text{Cl}$ was synthesized from HLCoCl (4) in the following manner. 216 mg sodium benzoate (1.50 mmol) and 164 mg $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (1.0 mmol) were added to a suspension of 260 mg HLCoCl (0.5 mmol) in 5.0 ml warm methanol. The mixture was refluxed until the reaction was observed to be complete by ¹H NMR spectroscopy (approximately 13 days). Yield 120 mg, 56%. *Anal.* Calc. for $\text{L}^{5\text{-Me}}\text{Co}_2(\text{O}_2\text{CC}_6\text{H}_5)\text{Cl} \cdot 0.5\text{H}_2\text{O}$, $\text{C}_{30}\text{H}_{25}\text{ClCo}_2\text{N}_2\text{O}_5$: C, 55.02; H, 3.82; N, 4.28. Found: C, 55.32; H, 4.08; N 4.85%. Other properties were in good agreement with those reported by Robson and co-workers for the analogous complex $\text{L}^{\text{Co}^{\text{II}}\text{Co}^{\text{III}}}(\text{OH})(\text{O}_2\text{CCH}_3)$ (6) [6].

Results and discussion

Synthesis and characterization of HLCoCl (4)

The tetramethylated ligand 2,6-bis{2-[(3,5-dimethyl-2-hydroxyphenyl)imino]methyl}-4-methylphenol, H_3L , (3) was utilized in place of Robson's ligand 1 for most studies, due to the increased solubility imparted by the additional methyl substituents. Condensation of the macroligand pieces in the presence of cobalt(II) chloride, followed by spontaneous air oxidation, led to the precipitation of a hydrated monocobaltic complex, 4, from solution.



The oxidation state of the cobalt was confirmed by ¹H NMR spectroscopy where a solution of 4 in methanol-d₄ exhibited a diamagnetic spectrum characteristic of

low spin cobalt(III) in an octahedral environment [8]. This diamagnetic character made NMR particularly useful for the characterization of the complex.

Proton assignments were made by two-dimensional homonuclear proton correlated experiments (2-D COSY) and were substantiated by comparison of the spectrum of 4 to those of the analogous monocobaltic complexes of 1 and the 4- and 5-methyl derivatized ligands, 2,6-bis{2-[(4-methyl-2-hydroxyphenyl)imino]methyl}-4-methylphenol and 2,6-bis{2-[(5-methyl-2-hydroxyphenyl)imino]methyl}-4-methylphenol (Table 1). The asymmetry of the complex was readily apparent from the identification of two separate sets of spin systems in the 2-D COSY spectrum. These spin systems were related through the central methyl group on the ligand which was not affected by loss of the C_{2v} symmetry axis. Each spin system corresponds to one side of an unsymmetrical complex, as depicted in structure 4.

A chloride ion is present in the complex and was detected by energy dispersive X-ray spectroscopy and confirmed by elemental analysis. The chloride ion may be bound directly to the metal center in the solid state, as has been observed in related complexes [9, 10], however, in solution the chloride appears to be present as a counterion. The molecular weight of complex 4 was determined commercially by vapor phase osmometry in DMF and was in good agreement with the ionic structure $[\text{HLCo}(\text{DMF})]^+\text{Cl}^-$.

Cyclic voltammetric measurements were performed on 4 in DMF solution with 0.1 M TBAH as the supporting electrolyte. One irreversible reduction couple was obtained and can be assigned to the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ couple. The separation between the potential for the cathodic peak current (-0.96 V versus SCE) and the potential for the anodic peak current (-0.37 V versus SCE) is very large ($\Delta E_p = 0.59 \text{ V}$), which hinders the proper determination of $E_{1/2}$. No significant improvement was obtained as the scan rate was varied. The irreversibility of the couple can be attributed to an EC mechanism.

TABLE 1 Isotropic proton shifts for HLCoCl (4)^a

Proton position ^b	Methyls	Spin system	
		A	B
1	2.33		
2		8.00	7.34
3		8.84	8.68
4		7.34	7.07
5	2.28, 1.73 ^c		
6		7.02	6.44
7	2.21, 1.65 ^c		

^aProton shifts in ppm relative to CD_3OD solvent as the standard. ^bNumbered proton positions as shown in structure 4. ^cMethyl position assignments are tentative

Formation of $LCo_2Cl(O_2CC_6H_5)$ (**5**) from $HLCOCl$ (**4**)

Formation of the dicobalt complex $LCo_2Cl(O_2CC_6H_5)$ (**5**) by incorporation of a second cobalt ion into the monocobalt complex did not proceed readily. The reaction reached completion only after 13 days of refluxing **4** with excess $CoCl_2$ and sodium benzoate in methanol. The identity of the final product was confirmed by comparison to the previously reported cobalt complexes $L'Co^{II}Co^{III}(OR)(O_2CCH_3)$ ($R = CH_3, H$) which exist as dimers of the form $[L'Co^{II}Co^{III}(OR)]_2(O_2CCH_3)_2$ (**6**) [5, 6]. Although these dicobalt products are essentially identical, they arose by quite different pathways. In the case of **6**, the ligand reacted with cobalt(II) acetate to immediately form a dicobaltous complex, **7**, which was then oxidized by dioxygen to form the mixed valent complex. The rapid formation of the dicobaltous complex is in stark contrast to the inertness of **4** towards retention of a second cobalt ion.

The key to this reactivity difference appears to be the availability of a carboxylate ligand which can bridge the cobalt centers, thus stabilizing the labile cobaltous ions. When an acetate ligand was supplied as part of the cobalt starting material a stable dicobaltous complex with a bridging acetate ligand was obtained. However, in the absence of a carboxylate ligand only one cobalt was retained by the macroligand.

Unlike the Schiff base ligand, complexation of two cobalt centers by the more highly dentate polypodal ligand **2** occurred readily [3]. These additional sites are pyridine donors which complement the nitrophilicity of cobalt and may provide stabilization in this manner as well. In addition, a *macrocyclic* Schiff base ligand has been shown to incorporate and maintain two cobalt(II) ions without external ligand assistance [11–13]. Like the polypodal ligand, this system provides four donor sites per cobalt ion and, in addition, can take advantage of the macrocyclic effect.

Oxidation of the cobalt centers

The polypodal and Schiff base ligands also differ in their ability to stabilize multiple cobalt(III) oxidation states. Under oxidizing conditions the Schiff base complex **5** formed as a stable, mixed valent $Co^{II}Co^{III}$ complex, however, the polypodal complex **8** proceeded to a stable dicobaltic species. The lack of further oxidation observed in **5** is likely due to insufficient nitrogen donor atoms to stabilize two cobalt(III) centers. The polypodal ligand **2**, which has an additional pyridine per cobalt in its donor set, was able to support two cobalt(III) centers [3], as was a related polypodal complex, 2,6-bis[bis(2-pyridylmethyl)amino)methyl]-4-methylphenol [14, 15].

In the case of **5**, no electrochemical generation of the dicobaltic form was observed by cyclic voltammetry in the potential range scanned (up to +1.5 V). Only reduction of the mixed-valence complex from $Co^{II}Co^{III}$

to $Co^{II}Co^{II}$ was observed as a half-couple (cathodic $E_p = -1.13$ V versus SCE) lacking the anodic current peak. As with the monocobalt complex **5**, this irreversibility is most likely due to an EC mechanism. Complex **8** also underwent similar irreversible reductions, as has been reported previously [3].

Conclusions

Reaction of the Schiff base ligand **3** with $CoCl_2 \cdot 2H_2O$ resulted in facile complexation and oxidation of one cobalt ion to form the monocobaltic complex **4**. Characterization of this unusual complex is reported. Complexation of two cobalt ions by ligand **3** was productive only in the presence of an exogenous carboxylate ligand. The oxidation of one cobalt center complexed to Schiff base ligand **3** occurred readily, however, oxidation of a second coordinated cobalt center was not observed. It is suggested that a deficiency of nitrogen donors prohibits **3** from effectively stabilizing the higher cobalt oxidation states.

Attempts are currently underway to access heterobimetallic complexes via the monocobalt complex **4** as well as to explore the reactions of the full set of diiron and dicobalt complexes of ligands **2** and **3**.

Acknowledgements

The support of this research by the National Science Foundation through ROW and EPSCoR grants is gratefully acknowledged. We also thank Andi Nelson of the Clemson University Electron Microscope Facility for assistance with the energy dispersive X-ray spectroscopy.

References

- 1 R. Robson, *Inorg. Nucl. Chem. Lett.*, **6** (1970) 125.
- 2 R. Robson, *Aust. J. Chem.*, **23** (1970) 2217.
- 3 V.D. Campbell, E.J. Parsons and W.T. Pennington, *Inorg. Chem.*, **32** (1993) 1773.
- 4 (a) S. Sandí-Ureña, *M.S. Thesis*, Clemson University, Aug. 1992, (b) S. Sandí-Ureña and E.J. Parsons, *Inorg. Chem.*, submitted for publication.
- 5 R. Robson and D.G. Vince, *Inorg. Chim. Acta*, **25** (1977) 191.
- 6 B.F. Hoskins, R. Robson and D. Vince, *J. Chem. Soc., Chem. Commun.*, (1973) 392.
- 7 S. Taniguchi, *Bull. Chem. Soc. Jpn.*, **57** (1984) 2683.
- 8 I. Bertini and C. Luchinat, *NMR of Paramagnetic Molecules in Biological Systems*, Benjamin/Cummings, Menlo Park, CA, 1986.
- 9 C. Fraser, L. Johnston, A.L. Rheingold, B.S. Haggerty, G.K. Williams, J. Whelan and B. Bosnich, *Inorg. Chem.*, **31** (1992) 1835.

- 10 E.D. McKenzie and J.M. Worthington, *Inorg Chim Acta*, 16 (1976) 9.
- 11 B.F. Hoskins, R. Robson and G.A. Williams, *Inorg. Chim Acta*, 16 (1976) 121.
- 12 N.H. Pilkington and R. Robson, *Aust J Chem*, 23 (1970) 2225.
- 13 B.F. Hoskins and G.A. Williams, *Aust. J Chem*, 28 (1975) 2607.
- 14 M. Suzuki, I. Ueda, H. Kanatomi and I. Murase, *Chem Lett*, (1983) 185
- 15 M. Suzuki, H. Kanatomi and I. Murase, *Chem Lett*, (1981) 1745.