Inorganica Chimica Acta 394 (2013) 203–209

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and characterization of binuclear Co(II) complexes with bis(salen-type) ligands

Minna T. Räisänen [a,*], Heikki Korpi [a], Markku R. Sundberg [a], Alexander Savin [b], Markku Leskelä [a], Timo Repo [a,*]

[a] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 Helsinki, Finland
[b] Low Temperature Laboratory, Aalto University, P.O. Box 15100, FI-00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 15 May 2012
Received in revised form 31 July 2012
Accepted 5 August 2012
Available online 28 August 2012

Keywords:
Binuclear Co(II) Schiff bases
Molecular modeling
O–O Activation
Alcohol oxidation

ABSTRACT

Two new, bridged bis(salen-type) ligand precursors, 1,1,3,3-tetrakis(salicylidene-3-iminopropyl)butylenediamine (**I**) and 1,1,3,3-tetra(salicylideneiminomethyl)propane (**IV**), were prepared by Schiff base condensation of salicylaldehyde with appropriate tetraamines. Corresponding binuclear Co(II) complexes **1** and **2** were obtained with moderate yields and the complexes were characterized in detail. Structural optimizations of the complexes were carried out at the B3LYP/6-311G* level of theory. Dioxygen coordination abilities of **1** and **2** were studied experimentally by UV–Vis spectroscopy and compared with traditional *N*,*N*′-ethylenebis(salicylideniminato)Co(II), Co(salen) (**3**). In addition, catalytic activities of **1** and **2** in comparison with various mononuclear salen-type Co complexes (**3**–**7**) were studied in the oxidation of 3,4-dimethoxybenzyl alcohol (veratryl alcohol) in alkaline aqueous solutions.

1. Introduction

Ability of synthesized transition metal complexes to activate dioxygen was initially observed by Tsumaki et al. in 1930's with *N*,*N*′-ethylenebis(salicylideniminato)Co(II) (Co(salen)) [1] and since then reversible activation of dioxygen has been studied with numerous metal complexes [2]. Salen-type complexes have been found to catalyze a variety of oxidation reactions, such as oxidation of phenols, sulfides, alcohols and lignin model compounds [2c,3]. The oxidation capability of the complexes can be further improved by altering the ligand framework by different substituents or by bridging metal centers to form a multinuclear complex. In fact, a significant amount of recent research has been focused on towards multinuclear transition metal complexes where closely adjacent metal centers may function co-operatively resulting in increased reaction rates in comparison to analogous mononuclear complexes [3a,4]. For example, when the two metal centers are coordinated at a suitable predetermined distance, they may have a tendency to coordinate and activate small molecules, such as dioxygen, between them [4c,f,5].

As an augmentation to our previous studies on Schiff base oxidation catalysts [6], we report herein the synthesis and characterization of two new [7] bimetallic Co(II) complexes (Fig. 1). Catalytic behavior of the complexes in oxidation of 3,4-dimethoxybenzyl alcohol (veratryl alcohol) is studied as well.

2. Experimental section

2.1. General methods and instrumentation

All reagents were purchased from Aldrich and used as received. The complexes were prepared and handled under argon atmosphere using standard Schlenk techniques. The products were characterized (when possible) with a Varian Gemini 200 spectrometer (200 MHz). Electron ionization (EI) mass spectra were run with a JEOL JMS-SX 102 mass spectrometer (ionizing voltage 70 eV) from solid samples and high resolution (HR) electrospray ionization time-of-flight (ESI-TOF) mass spectra were run with a Bruker micrOTOF mass spectrometer from methanol–acetonitrile solutions. Fast atom bombardment (FAB) mass spectrometry measurements were carried out with a Finnigan MAT TSQ-7000 instrument at the University of Ulm, Germany. FT-IR spectra were recorded from neat samples pressed against a diamond window using a Perkin Elmer Spectrum One spectrometer. For the far-IR measurements with a Perkin Elmer Spectrum GX spectrometer, polyethylene pellets of the compounds were prepared. UV–Vis spectra were recorded with a Hewlett Packard 8453 spectrophotometer from methanol (**I** and **1**) or chloroform (**IV** and **2**) solutions. Magnetic measurements were performed for powdered samples mixed with stycast epoxy using a Quantum Design

---

* Corresponding authors. Fax: +358 9 191 50198.
E-mail addresses: minna.t.raisanen@helsinki.fi (M.T. Räisänen), timo.repo@helsinki.fi (T. Repo).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2012.08.007

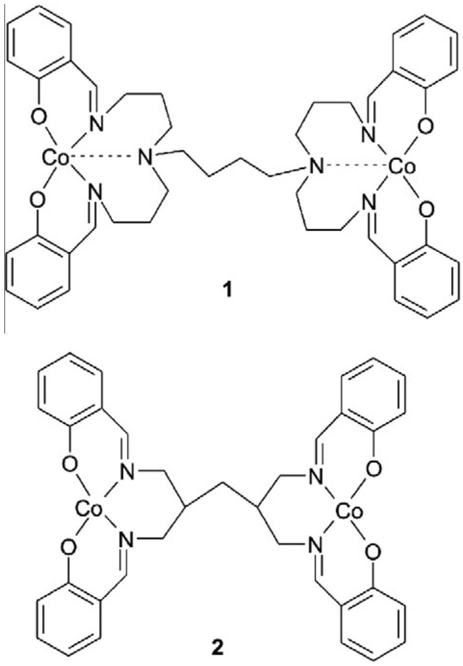


Fig. 1. Synthesized binuclear Co(salen) complexes **1** and **2**.

MPMS-XL SQUID magnetometer. The SQUID outputs were corrected for sample holder and stycast magnetizations. Diamagnetic corrections were carried out using Pascal's constants. The magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{½}$. Oxidation products were analyzed with an Agilent Technologies 6890 N gas chromatograph.

2.2. Computational details

The initial coordinates for the complexes **1** and **2** were obtained by Spartan [8] optimizations at semiempirical level (PM3). The output coordinates were then used as input for the optimizations carried out by GAUSSIAN03 program suite [9] at the B3LYP/6-311G* level. Since the experimental magnetic measurements clearly indicated that there are three unpaired electrons at each cobalt atom, only the spin multiplicity of seven was utilized in the subsequent optimizations.

2.3. Oxidation experiments

For the oxidation experiments, 10 mL of 0.05 M NaOH solution (pH 12.6), veratryl alcohol (0.2 mL, 1.377 mmol) and the catalyst (1:40 M ratio of metal and veratryl alcohol, 17.2 μmol of binuclear and 34.4 μmol of mononuclear complexes) were mixed in a glass vessel fitted inside a steel autoclave. O_2-pressure of 10 bar was then applied and the autoclave was set in an oil bath (80 °C) for 20 h. After cooling to ambient temperature, the solution was extracted with ethyl acetate and analyzed with gas chromatography. Activity of the catalysts is expressed as a percentage of formed veratraldehyde, which was the only product observed. Each oxidation experiment was done twice and the reported values refer to the average values.

2.4. Synthesis

Complex **3** was purchased from Aldrich and used without further purification, whereas 1,1,3,3-tetracarboxamidopropane (**II**) and complexes **4**–**7** were prepared according to literature methods [10].

Table 1
The main bands (cm^{-1}) in the IR spectra of ligand precursors **I** and **IV** and complexes **1** and **2**.

	I	1	IV	2
ν(C=N), s	1630	1630	1629	1625
ν(C=C, arom.), m	1579	1599	1578	1571
δ(CH_2), m	1497	1466	1500	1471
ν(C–C), s	–	1446	–	1448
ν(C–O, phenol), s	1284	1307	1276	1300
ν(C–N, tert. amine), m	1147	1152	–	–
ν(Ar–H), s	1113	1126	–	–
ν(Co–N)	751	757	754	752
	–	474	–	471
	–	444	–	–
ν(Co–O)	–	346	–	324
	–	292	–	279

s = strong, m = medium.

Table 2
Oxidation studies of veratryl alcohol with Co(II) salen-type complexes **1**–**7** with different *N,N'*-bridge structures.

Complex	Aldehyde conversion (%)
1	4
2	13
3	93
4	7
5	0
6	77
7	46

The reaction conditions: veratryl alcohol (0.2 mL, 1.377 mmol), 0.05 M NaOH solution (pH 12.6), 80 °C, O_2-pressure 10 bar, 1:40 M ratio of metal and veratryl alcohol, reaction time 20 h.

2.4.1. 1,1,3,3-Tetrakis(salicylidene-3-iminopropyl)butylenediamine (*I*), H_4L^1

Compound **I** was prepared by a condensation reaction of commercial DAB-Am-4 (polypropylenimine tetraamine dendrimer) (4.00 g, 12.6 mmol) and salicylaldehyde (6.17 g, 50.5 mmol). The starting materials were mixed (1:4 M ratio) in EtOH (20 mL) and stirred at 50 °C for 2 h. The mixture was cooled and two yellow phases were separated. Lower oily phase was dissolved in $CHCl_3$–EtOH (1:1) in which the product (8.00 g, 87%) crystallized overnight at −10 °C. Mp. 54–56 °C. *Anal.* Calc. for $C_{44}H_{56}N_6O_4$: C, 72.10; H, 7.70; N, 11.47. Found: C, 72.45; H, 7.89; N, 11.71%. EI-MS *m*/*z* 732, M^+. ^1H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): $\delta = 1.39$ (s, CH_2, 4H), 1.80 (qv, CH_2, $^3J_{HH} = 6.8$ Hz, 8H), 2.39 (s, CH_2, 4H), 2.49 (t, CH_2, $^3J_{HH} = 7.4$ Hz, 8H), 3.60 (t, CH_2, $^3J_{HH} = 6.8$ Hz, 8H), 6.79–6.96 (m, H–Ar, 8H), 7.18–7.32 (m, H–Ar, 8H), 8.31 (s, CH=N, 4H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 25.35$ ($2CH_2$), 28.68 ($4CH_2$), 51.59 ($4CH_2$, –N–C–), 54.15 ($2CH_2$, –N–C–), 57.60 (CH_2, =N–C), 117.18, 118.61, 118.97, 131.31, 132.24, 161.49 (C_6H_4), 165.04 (4CH, C=N) ppm. HR ESI-TOF MS *m*/*z* (%): 394 (69); 733 (24), $[M+H]^+$ (calc. 733.4436; found 733.4417; error 2.54 ppm); 755 (100), $[M+Na]^+$. For IR and UV–Vis data, see Tables 1 and 2.

2.4.2. 1,1,3,3-Tetra(methylamine)propane (*III*)

Compound **III** was prepared by reduction of 1,1,3,3-tetracarboxamidopropane (**II**). Fresh BH_3.THF (1 M, 200 mL) was slowly added over 1 h to a THF (40 mL) suspension of **II** (5.0 g, 23.1 mmol). Reaction vessel was kept in an ice bath during the addition and once the addition was complete, the mixture was refluxed overnight. The reaction mixture was cooled to ambient temperature and the excess of borane was destroyed by cautious addition of H_2O (20 mL). The solution was evaporated to dryness and slowly treated with 5 M HCl (100 mL). Resulting mixture was refluxed for 1 h and then taken to dryness. Obtained white residue was dissolved in H_2O (50 mL) and 5 M NaOH (40 mL) was added. The solution was stirred for 30 min and evaporated to dryness. The obtained white product contained residues from borane, HCl and NaOH but it could be used for the further reactions without purification. The product is water-soluble but only moderately soluble in DMSO, MeOH and EtOH. ^{1}H NMR (200 MHz, CD_3OD, 25 °C): $\delta = 1.23$ (t, CH_2, $^3J_{HH} = 6.8$ Hz, 2H), 1.50–1.62 (m, 2H, CH), 2.67 (d, CH_2, $^3J_{HH} = 5.8$ Hz, 8H) ppm.

2.4.3. *1,1,3,3-Tetra(salicylideneiminomethyl)propane (**IV**), H_4L^2*

When salicylaldehyde was added dropwise in EtOH suspension of **III**, the solution turned immediately yellow. The reaction mixture was stirred at 60 °C for 2 h and filtered. Liquid phase was evaporated to dryness and residue was treated with $CHCl_3–H_2O$ (1:1, 40 mL). Water phase was washed with $CHCl_3$ (20 mL) and extracts were added to the previous organic phase. Combined $CHCl_3$ phase was dried with Na_2SO_4, filtered, and the solvent was evaporated. Crystallization of the product from EtOH–$CHCl_3$ (1:1) gave yellow needles. Mp. 166–168 °C. *Anal.* Calc. for $C_{35}H_{36}N_4O_4{\cdot}H_2O$: C, 70.69; H, 6.44; N, 9.42; O, 13.45. Found: C, 70.64; H, 6.04; N, 9.37; O, 13.29%. EI-MS *m/z* 576, M$^+$. ^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): $\delta = 1.57$ (t, $^3J_{HH} = 7.0$ Hz, 2H, CH_2), 2.34 (qv, $^3J_{HH} = 6.1$ Hz, 2H, CH), 3.69 (d, $^3J_{HH} = 5.6$ Hz, 8H, CH_2), 6.81–6.96 (m, 8H, H–Ar), 7.18–7.35 (m, 8H, H–Ar), 8.35 (s, 4H, CH=N) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, TMS, 25 °C): $\delta = 31.38$ (CH_2), 37.84 (2CH), 61.14 ($4CH_2$), 116.90, 118.65, 118.71, 131.46, 132.38, 161.00 (C_6H_4), 166.27 (4CH, C=N) ppm. HR ESI-TOF MS *m/z* (%): 496 (68); 577 (90), [M+H]$^+$ (calc. 577.2809; found 577.2796; error 2.23 ppm); 599 (100), [M+Na]$^+$. For IR and UV–Vis data, see Tables 1 and 2.

2.4.4. *Co(II) complexes **1** and **2***

Complexation reactions of **1** and **2** were carried out in a similar way. Ligand was dissolved in absolute EtOH (20 mL) and two equivalents of Co(II) acetate were added. Color of the reaction mixture changed immediately and the complex started to precipitate. The reaction mixture was stirred at 70 °C for 20 h and filtered before cooling to ambient temperature.

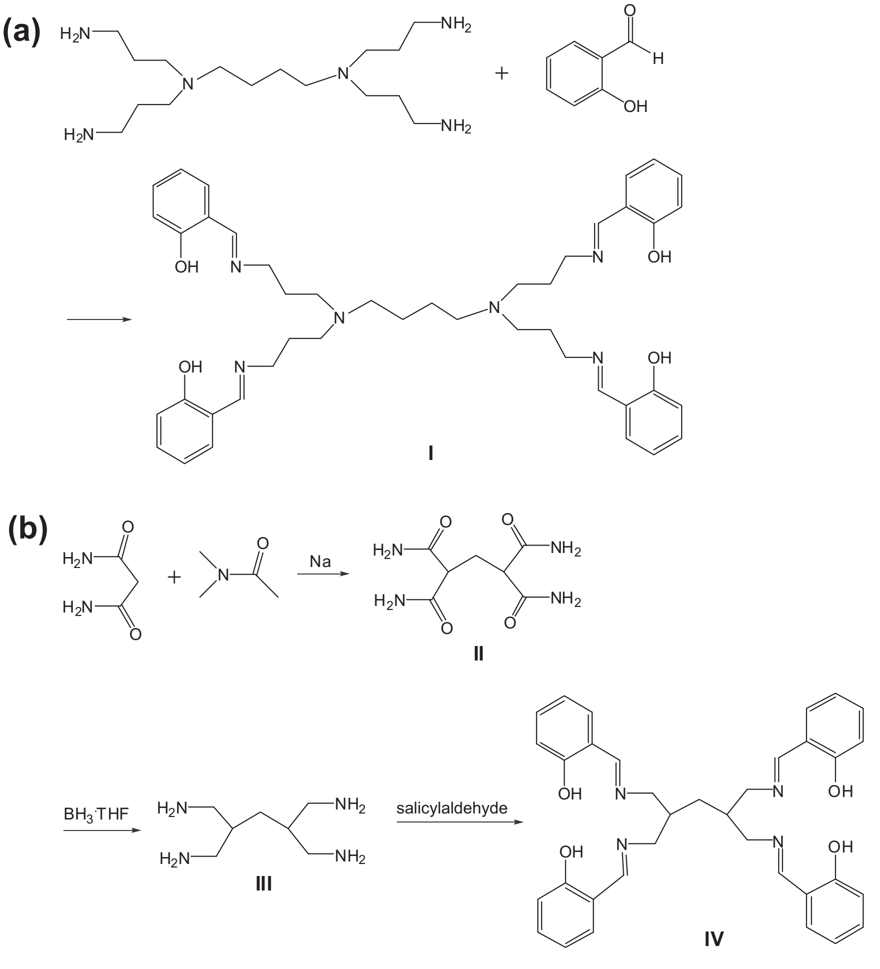
*Co(II)$_2$L^1 (**1**):* Reaction of ligand **I** (1.00 g, 1.36 mmol) and $Co(OOCCH_3)_2{\cdot}4H_2O$ (0.68 g, 2.72 mmol) gave a brown product, which was filtered (0.69 g, 56%). *Anal.* Calc. for $C_{44}H_{52}N_6O_4Co_2{\cdot}1.5H_2O$: C, 60.48; H, 6.34; N, 9.62; O, 10.07. Found: C, 60.98; H, 6.16; N, 9.40; O, 10.42%. FAB-MS *m/z* 846, M$^+$. HR ESI-TOF MS *m/z* (%): 846, M$^+$ (calc. 846.2709, found 846.2675, error 3.95 ppm). For IR and UV–Vis data, see Tables 1 and 2.

*Co(II)$_2$L^2 (**2**):* Reaction of ligand **IV** (1.00 g, 1.73 mmol) and $Co(OOCCH_3)_2{\cdot}4H_2O$ (0.86 g, 3.46 mmol) gave a brown product which was washed with $CHCl_3$ after filtration (0.50 g, 42%). *Anal.* Calc. for $C_{35}H_{32}N_4O_4Co_2{\cdot}3H_2O$: C, 56.46; H, 5.14; N, 7.52; O, 15.04. Found: C, 56.51; H, 5.01; N, 7.60; O, 15.16%. EI-MS *m/z* 691, M$^+$. HR ESI-TOF MS *m/z* (%): 690, M$^+$ (calc. 690.1082; found 690.1065; error 2.50 ppm). For IR and UV–Vis data, see Tables 1 and 2.

3. Results and discussion

3.1. *Syntheses*

Ligand precursor **I** was prepared from commercially available starting materials by a one-step Schiff base condensation reaction. Ligand precursor **IV** was synthesized with a three-step synthesis



Scheme 1. Synthesis strategies for (a) 1,1,3,3-tetrakis(salicylidene-3-iminopropyl)-butylenediamine (**I**) and (b) 1,1,3,3-tetra(salicylideneiminomethyl)propane (**IV**).

where the reduction of tetracarboxamidopropane (**II**) to corresponding tetra(methylamine)propane (**III**) was problematic and thus decreased the total yield (Scheme 1). In order to improve the yields of bimetallic complexes **1** and **2** and avoid formation of mononuclear complex instead, reaction mixtures were heated overnight after which soluble impurities were separated by filtration from the hot reaction mixture. Complexes **1** and **2** were isolated in moderate yields as brown powders.

3.2. Characterization

Complexes **1** and **2** were characterized by elemental analysis and different spectroscopic and mass spectrometric techniques. Complexes **1** and **2** are paramagnetic at 300 K with μ_{eff} values of 6.35 and 6.08 B.M., respectively. These values are significantly larger than the spin only value of two Co(II) ions with $S = 3/2$ (5.48 B.M. with $g = 2$) but in the range expected for high-spin binuclear complexes [11].

In the IR spectra of salen ligand precursors **I** and **IV** (Table 1), C=N, phenolic C–O and aromatic C=C stretching vibrations are on the regions usually observed in Schiff bases [12]. The aromatic C–H vibration is observed in the region of 750 cm^{-1}, which is assigned for aromatic rings with four adjacent hydrogen atoms. Upon complex formation, the C=N, C–O and C=C vibrations are shifted and their intensities are changed. For example, the C–C vibrations of the complexes are notably stronger than those of the ligands. In complex **1**, the tertiary amine in the bridge coordinates to cobalt ion causing the C–N vibration to shift in 1100–1150 cm^{-1} region. The metal–ligand vibrations are observed in the region of <700 cm^{-1}. According to far-IR data of Schiff base complexes, M–O and M–N vibrations appear in 270–330 and 410–450 cm^{-1} regions, respectively [12b]. Aromatic ring vibrations observed in 450 cm^{-1} region in the ligand spectra fade upon the complexation and new bands of the chelate rings are observed in 550–600 cm^{-1} region.

In the electronic spectra of **I** and **IV**, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are at 214–315 nm and *ca.* 405 nm regions, respectively [12c,13]. Upon formation of complexes **1** and **2**, the $\pi \rightarrow \pi^*$ transitions appear at 213–314 nm region in the spectra recorded under protective gas. In the spectra of **1** and **2** the $n \rightarrow \pi^*$ and $d \rightarrow d$ transitions appear at *ca.* 405 nm and at 624–660 nm regions, respectively, with weak intensities. The $d \rightarrow d$ transitions suggest that the geometries around Co(II) centers of the complexes in solution are the same as in their solid forms.

Abilities of binuclear complexes **1** and **2**, and mononuclear Co(salen) complex **3** as a comparison, to coordinate O_2 were studied experimentally by UV–Vis spectroscopy from 0.1 mM DMF solutions using pyridine as a base. Both **1** and **3** coordinated O_2 reversibly at room temperature but the former considerably slower than the latter. Whereas **3** coordinates O_2 within minutes when air is bubbled through the solution, **1** must be in air contact overnight before similar changes can be seen in the spectrum (Fig. 2). The O_2 coordination and subsequent desorption by argon gas were done twice. As expected, raise of the reaction temperature to 80 °C seems to be unfavorable for the coordination of O_2 [14] as complex **1** was not observed to coordinate O_2 at that temperature during the period of 18 h. In similar experiments with **2** at ambient temperature the O_2 coordination was found to be irreversible. This behavior has been previously observed for example with the mononuclear analog of complex **1** [15]. After one day exposure to air, the $\pi \rightarrow \pi^*$ transition of **2** is red shifted from 272 nm to 287 nm and a new absorption band at 399 nm assignable to $d \rightarrow \pi^*$ transition appears. Transitions $n \rightarrow \pi^*$ and $d \rightarrow d$ are too weak to be observed. The increased intensity of the $d \rightarrow \pi^*$ transition upon oxygen adduct formation has been previously reported in the literature for *N*,*N*′-(*o*-phenylene)bis(salicylideneiminato)Co(II) (**7**) [13b]. For more details about O_2 coordination abilities of Co Schiff bases with different ligand structures in nonaqueous solution see the study of Pui [16].

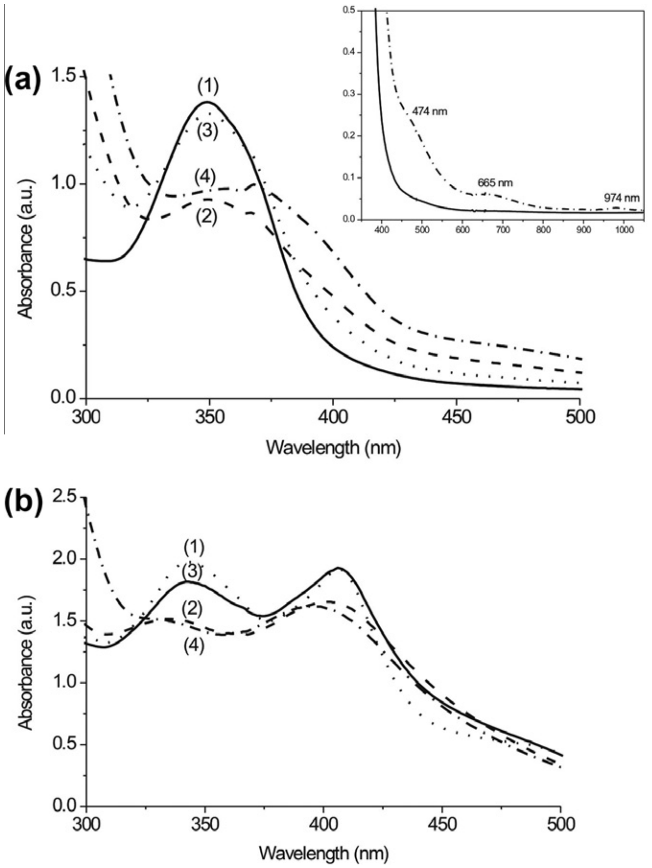


Fig. 2. UV–Vis spectra of complexes (a) **1** and (b) **3** in DMF (pyridine as an axial base) in the range of 300–500 nm. Spectra (1) have been recorded from a cooled solution that was heated at 100 °C for 15 min with a continuous argon flow, spectra (2) after an overnight exposure to air, spectra (3) after a second argon treatment and spectra (4) after another overnight exposure to air. In the inset of (a) is shown the 350–1050 nm region of spectra (1) (solid line) and (4).

The bands at about 292, 343, 406 and 489 nm (shoulder) in the spectrum of **3** recorded under protective gas can be assigned to

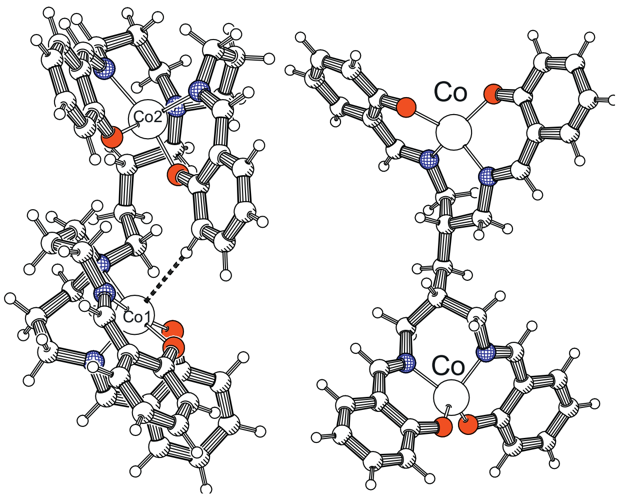


Fig. 3. Optimized structures of complexes (a) **1** and (b) **2** at the B3LYP/6-311G* level of theory. In **1** the Co1–H92 interaction is indicated by a dashed line. Color code: O, red; N, blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

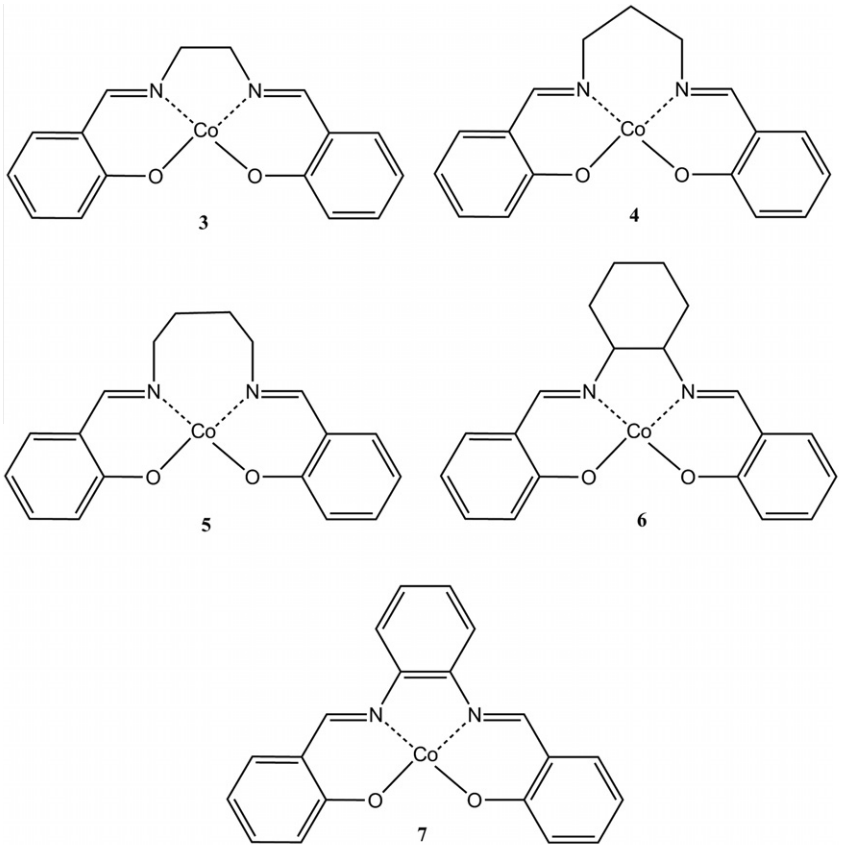


Fig. 4. Mononuclear Co(II) salen-type complexes **3**–**7** with different *N,N′*-bridge structures for oxidation studies of veratryl alcohol.

$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $d \rightarrow \pi^*$ and $d \rightarrow d$ transitions, respectively [13,15,17]. In the respective spectrum of **1** $\pi \rightarrow \pi^*$ (286 nm) and $d \rightarrow \pi^*$ (349 nm) transitions are blue shifted compared to those of **3** whereas $n \rightarrow \pi^*$ and $d \rightarrow d$ transitions are too weak to be observed. The shifts are probably due to the $-(CH_2)_3N(CH_2)_3-$ bridge between the two imine groups which donates more electron density to the Co^{2+} ion than the, respective ethylene bridge of **3** [13a]. Upon exposure to air, the $\pi \rightarrow \pi^*$ transitions of **1** and **3** have not shifted but their intensities have changed. In the case of **1**, $d \rightarrow \pi^*$ transition is splitted into two bands at 349 and 367 nm which suggests that the Co^{3+} centers are monobridged by O_2, i.e. μ-peroxo complex is formed [14a,18; for crystal structure of μ-peroxo complex formed from two mononuclear species similar to complex **1** see Ref. 19]. The oxygenated form of **1** shows new weak bands at 474 nm (shoulder) and 665 nm which are also likely to be $d \rightarrow \pi^*$ transitions [14a]. A new band at 974 nm is assignable to $d \rightarrow d$ transition and implies octahedral geometry around the metal centers [20]. In the case of **3**, $n \rightarrow \pi^*$ and $d \rightarrow \pi^*$ transitions are blue shifted upon exposure to air.

3.3. Structural modeling

Despite of our efforts, single crystals suitable for X-ray crystal structure determination were not obtained for **1** and **2**. Therefore, the structures were optimized at the B3LYP/6-311G* level of theory (Fig. 3). In the dinuclear complex **1** the cobalt atoms are seemingly five-coordinated. The coordination polyhedra resemble distorted square pyramids with a nitrogen atom in the axial position. The τ value for Co1 and Co2 coordination polyhedra is 0.03, indicating that the distortion is almost negligible, since the value for ideal square pyramid is 0 [21]. The Co–N bonds are systematically longer than the Co–O bonds and the axial Co–N bond is shorter than the equatorial Co–N bonds. Although formally similar, the two chromophores are different. This is clearly seen in the orientation of the aromatic rings. Related with this, there is hydrogen atom H92 pointing towards Co1, whereas there is no similar hydrogen in the vicinity of Co2. The Co1–H92 distance is 2.778 Å, which excludes existence of normal covalent bond. However, QTAIM analysis found a bond critical path between Co1 and H98. Therefore, we may also describe the coordination polyhedron as distorted octahedron. A similar bond path was not found for Co2.

Also in complex **2** both coordination spheres display the same type coordination polyhedron, namely tetrahedron. This is in sharp contrast with the previous case, where the Co(II) cations are five-coordinated. The difference is due to the different number of available ligand atoms. Again, the Co–N bond lengths are longer than the Co–O bond lengths in the two chromophores. The coordination polyhedra are distorted, which can be seen in the bond angles. It should be noted here, that square-planar Co(II) complexes should have magnetic moments in the range of 2.2–2.7 B.M. per metal center [22]. Our experimental value of 4.3 B.M./Co(II) is clearly bigger and is in accordance with the values observed in the literature for tetrahedral Co(II) complexes [17b,23]. Thus the experimental results support the optimized geometry of distorted tetrahedron.

3.4. Oxidation experiments

Due to the inherent complexity of lignin, small and structurally define model compounds, such as veratryl alcohol, are needed for efficient evaluation of catalyst candidates. The ability of binuclear complexes **1** and **2** to catalyze the oxidation of veratryl alcohol [24] to veratraldehyde under alkaline (pH 12.6) water solutions at 80 °C[1] [25] was studied and their catalytic properties were compared with a series of mononuclear complexes **3**–**7** (Fig. 4). The reaction conditions, under which the studied complexes were moderately soluble, were selected on the basis of our earlier experiments wherein the reaction conditions were optimized for **3** [6a,b]. The reaction mechanism is expected to be similar to the previously reported one: The oxidation cycle begins with a formation of μ-hydroxy bridges between two Co(II) centers followed by deprotonation of veratryl alcohol and formation of Co(II)- alkoxo intermediate. In the presence of oxygen, the metal centers of the intermediates are oxidized to Co(III) and μ-peroxo bridges are formed between them. In the final stage of the catalytic cycle, veratraldehyde molecules are formed and metal centers are reduced back to hydroxy-bridged Co(II) [26].

Even though **1** and **2** are capable to coordinate O_2, as indicated here by the UV–Vis measurements, they gave low aldehyde conversions, 4% and 13%, respectively (Table 2). However, these conversions are in the same range as achieved with mononuclear complexes **4** and **5** (0% and 7%, respectively). Since other mononuclear complexes (**3**, **6** and **7**) yielded significantly higher conversions (93%, 77%, and 46%, respectively), the reason for different activities is suggested to be related to the *N,N′*-bridge structure. In fact, the results underline that the activity of salen catalyst is decreased when the bridge consists of more than two carbon atoms. Indeed, **2** has the same coordination sphere with N_2O_2-donor atoms as the classical salen complex **3**, but its bridge structure is different consisting of three methylene-units instead of two. As a consequence, **2** has similar activity as **4** and **5** in this study. On the other hand, in **1** the Co(II) ion is coordinated by N_3O_2-ligand resulting in an additional nitrogen atom that is attached to the rigid ligand frame. According to our previous studies, the axial base should be mobile in order to enhance the dioxygen activation by the cobalt center in aqueous solution [6a,b].

A view on the published X-ray structures shows that the most active complexes (**3**, **6**, and **7**) from the studied ones have an approximately planar geometry around the Co(II) ion [27]. When the number of methylene-groups in the *N,N′*-bridge is more than two, the planar geometry changes closer to a tetrahedral [28] as in the case of **2** (Fig. 3). In addition, for example **1** has a square-pyramidal geometry (Fig. 3) and the mononuclear version of complex **1** a distorted trigonal–bipyramidal environment around the Co(II) center [29]. It seems that to activate oxygen, Co(salen) complexes need to have a planar geometry around the metal, which is accomplished here by the bridges consisting of two carbon atoms. Nishinaga et al. [30] have studied the same complexes (**3**, **5**–**7**) in catalytic dehydrogenation of secondary amines and have come to a similar conclusion.

4. Conclusions

Two new homobinuclear Co(II) salen-type complexes (**1** and **2**) were synthesized and fully characterized by several methods. Magnetic measurements showed that both **1** and **2** are high-spin complexes at 300 K with μ_{eff} values of 6.35 B.M. and 6.08 B.M., respectively. The values suggest square-pyramidal/trigonal–bipyramidal and tetrahedral geometry around the Co(II) centers in **1** and **2**, respectively, which are in accordance with the modeled structures. In the optimized structure of **1**, the Co(II) centers are in nearly square-pyramidal coordination spheres whereas in 2 they are in tetrahedral geometry. UV–Vis spectroscopic studies showed that complex **1** is capable of reversible O_2 coordination at 298 K in DMF with pyridine as base, whereas **2** exhibits an irreversible coordination. Despite of their O_2 coordination ability, the complexes showed low catalytic activities in the oxidation of veratryl alcohol in basic aqueous solutions with O_2 as oxidant.

Acknowledgments

The financial support of the Academy of Finland is gratefully acknowledged by MTR (251531), HK, ML and TR (209739). MRS acknowledges the generous computational resources provided by CSC (CSC — IT Center for Science Ltd).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.08.007.

References

[1] (a) P. Pfeiffer, E. Breith, E. Lübbe, T. Tsumaki, Liebigs Ann. Chem. 503 (1933) 84;
(b) T. Tsumaki, Bull. Chem. Soc. Jpn. 13 (1938) 527.
[2] (a) E. Niederhoffer, J. Timmons, A.E. Martell, Chem. Rev. 84 (1984) 137;
(b) J.P. Collman, R. Boulatov, C.J. Sunderland, L. Fu, Chem. Rev. 104 (2004) 561;
(c) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329;
(d) M.R. Tiné, Coord. Chem. Rev. 256 (2012) 316.
[3] (a) K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420;
(b) K.C. Gupta, A.K. Sutara, C.-C. Lin, Coord. Chem. Rev. 253 (2009) 1926;
(c) S.R. Collinson, W. Thielemans, Coord. Chem. Rev. 254 (2010) 1854.
[4] (a) P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 252 (2008) 1871;
(b) P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 248 (2004) 1717;
(c) L.G. Farrugia, P.A. Lovatt, R.D. Peacock, J. Chem. Soc., Dalton Trans. (1997) 911;
(d) N. Guo, L. Li, T.J. Marks, J. Am. Chem. Soc. 126 (2004) 6542;
(e) C. Belle, J.-L. Pierre, Eur. J. Inorg. Chem. (2003) 4137;
(f) M. Suzuki, H. Furutachi, H. Ōkawa, Coord. Chem. Rev. 200–202 (2000) 105.
[5] A.L. Gavrilova, B. Bosnich, Inorg. Chim. Acta 352 (2003) 24.
[6] (a) K. Kervinen, P. Lahtinen, T. Repo, M. Svahn, M. Leskelä, Catal. Today 75 (2002) 183;
(b) K. Kervinen, H. Korpi, T. Repo, M. Leskelä, J. Mol. Catal. A: Chem. 203 (2003) 9;
(c) J. Ahmad, P. Figiel, M. Räisänen, M. Leskelä, T. Repo, Appl. Catal. A 371 (2009) 17;
(d) P.J. Figiel, A. Sibaouih, J.U. Ahmad, M. Nieger, M.T. Räisänen, M. Leskelä, T. Repo, Adv. Synth. Catal. 351 (2009) 2625;
(e) J.U. Ahmad, M.T. Räisänen, M. Leskelä, T. Repo, Appl. Catal. A 411–412 (2012) 180;
(f) J.U. Ahmad, M.T. Räisänen, M. Kemell, M.J. Heikkilä, M. Leskelä, T. Repo, Appl. Catal. A., submitted for publication.
[7] The use of complex 1 has been reported in J. Martinovic, A.-M. Chiorcea-Paquim, V.C. Diculescu, J. Van Wyk, E. Iwuoha, P. Baker, S. Mapolie, A.-M. Oliveira-Brett, Electrochim. Acta 53 (2008) 4907. but no analyses of the compound have been presented.
[8] SPARTAN '02, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612, USA. <http://www.wavefun.com>.
[9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision D.02, GAUSSIAN, Inc., Wallingford, CT, 2004.
[10] (a) R.M. McAllister, J.H. Weber, J. Organomet. Chem. 77 (1974) 91;
(b) M. Hariharan, F.L. Urbach, Inorg. Chem. 8 (1969) 556;
(c) J. Manassen, Inorg. Chem. 9 (1970) 966;
(d) D. Chen, A.E. Martell, Y. Sun, Inorg. Chem. 28 (1989) 2647;
(e) H.C. Haas, A. Mass, R.D. Moreau, N.H. Nashua, US-4,227,013, October 7, 1980;
(f) H.C. Haas, R.D. Moreau, J. Polym. Sci. Polym. Chem. Ed. 16 (1978) 699.
[11] N. Torihara, H. Okawa, S. Kida, Bull. Chem. Soc. Jpn. 51 (1978) 3236.
[12] (a) A. Pui, I. Berdan, I. Morgenstern-Badarau, A. Gref, M. Perree-Fauvet, Inorg. Chim. Acta 320 (2001) 167;
(b) E. Szlyk, A. Surdykowski, M. Barwiolek, E. Larsen, Polyhedron 21 (2002) 2711;
(c) R.C. Felicio, E.T.G. Cavalheiro, E.R. Dockal, Polyhedron 20 (2001) 261.

---

[1] In this reaction, the main oxidation product is typically verataldehyde but traces (<1%) of veratric acid have been observed with high aldehyde conversions.

[13] (a) K.C. Gupta, H.K. Abdulkadir, S. Chand, J. Mol. Catal. A: Chem. 202 (2003) 253;
(b) B. Ortiz, S.-M. Park, Bull. Korean Chem. Soc. 21 (2000) 405.
[14] (a) V.M. Miskowski, J.L. Robbins, I.M. Treitel, H.B. Gray, Inorg. Chem. 14 (1975) 2318;
(b) D.V. Stynes, H. Cleary Stynes, J.A. Ibers, B.R. James, J. Am. Chem. Soc. 95 (1973) 1142;
(c) A. Huber, L. Müller, H. Elias, R. Klement, M. Valko, Eur. J. Inorg. Chem. (2005) 1459.
[15] E.V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D.H. Busch, Inorg. Chem. 36 (1997) 2746.
[16] A. Pui, Croat. Chem. Acta 75 (2002) 165.
[17] (a) C.J. Hipp, W.A. Baker, J. Am. Chem. Soc. 92 (1970) 792;
(b) L. Sacconi, M. Ciampolini, F. Maggio, F.P. Cavasino, J. Am. Chem. Soc. 84 (1962) 3246.
[18] A.B.P. Lever, H.B. Gray, Acc. Chem. Res. 11 (1978) 348.
[19] L.A. Lindblom, W.P. Schaefer, R.E. Marsh, Acta Crystallogr., Sect. B 27 (1971) 1461.
[20] A.K. Singh, Sanyucta Kumari, T.N. Guru Rowb, Jai Prakash, K. Ravi Kumar, B. Sridhar, T.R. Rao, Polyhedron 27 (2008) 3710.
[21] (a) A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349;
(b) C. Adamo, V. Barone, J. Chem. Phys. 108 (1998) 664;
(c) J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533;
(d) J.J.P. Stewart, J. Comput. Chem. 10 (1989) 221;
(e) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[22] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, third ed., Interscience Publishers, New York, 1972.
[23] M. Shebl, Spectrochim. Acta, Part A 73 (2009) 313.
[24] (a) M. Balakshin, C. Chen, J. Gratzl, A. Kirkman, H. Jakob, Holzforschung 54 (2000) 171;
(b) R. ten Have, P. Teunissen, Chem. Rev. 101 (2001) 3397.
[25] P. Lahtinen, H. Korpi, E. Haavisto, T. Repo, M. Leskelä, J. Comb. Chem. 6 (2004) 967.
[26] K. Kervinen, H. Korpi, J.G. Mesu, F. Soulimani, T. Repo, B. Rieger, M. Leskelä, B.M. Weckhuysen, Eur. J. Inorg. Chem. (2005) 2591.
[27] (a) W. Schaefer, R. Marsh, Acta Crystallogr., Sect. B 25 (1969) 1675;
(b) N. Bresciani, M. Calligaris, G. Nardin, L. Randaccio, J. Chem. Soc., Dalton Trans. (1974) 1606;
(c) N.B. Pahor, M. Calligaris, P. Delise, G. Dodic, G. Nardin, L. Randaccio, J. Chem. Soc., Dalton Trans. (1976) 2478.
[28] S. Yamada, Coord. Chem. Rev. 190–192 (1999) 537.
[29] P. Zanello, R. Cini, A. Cinquantini, P.L. Orioli, J. Chem. Soc., Dalton Trans. (1983) 2159.
[30] A. Nishinaga, S. Yamazaki, T. Matsuura, Tetrahedron Lett. 29 (1988) 4115.