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Oxygenation of heterodinuclear di(μ-phenoxo) $Co^{II}M^{II}$ (M = Mn, Fe or Co) complexes having a "Co(salen)" entity in a macrocyclic framework †

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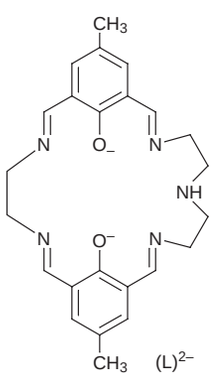
Heterodinuclear di(μ-phenoxo) $Co^{II}M^{II}$ complexes $[CoM(L)(AcO)]ClO_4$ (M = Mn **1**, Fe **2** or Co **3**) and $[CoM(L)(NCS)]ClO_4$ (M = Mn **4**, Fe **5** or Co **6**) have been obtained where L^{2-} is a heterodinucleating macrocycle derived by the 2 : 1 : 1 condensation of 2,6-diformyl-4-methylphenol, ethylenediamine and diethylenetriamine and has a "salen"-like N_2O_2 metal-binding site and a "saldien"-like N_3O_2 site sharing the phenolic oxygens. The CoM(AcO) complexes **1** and **3** show reversible oxygenation at 0 °C in dmf, whereas **2** is irreversibly oxidized under the same conditions. The structures of the dioxygen adducts of **1** and **3** have been determined by X-ray crystallography. In that of **1**, $[\{CoMn(L)(AcO)\}_2(O_2)][ClO_4]_2\cdot 4CH_3CN$ oxy-**1**, the Co resides in the "salen" site and the Mn in the "saldien" site. An exogenous acetate group bridges the two metal ions in the $\eta^1:\eta^1$ mode together with the two phenolic oxygens. The peroxo group bridges two {CoMn(L)(AcO)} molecules at the Co forming a Co–O–O–Co linkage. The peroxo O(1)–O(2) bond distance is 1.416(5) Å and the Co(1) · · · Co(2) intermetallic separation is 4.359(1) Å. The geometry about the Co is pseudo octahedral with a peroxo oxygen and an acetate oxygen at the axial sites and the Mn has a distorted six-co-ordination. The dioxygen adduct of **3**, $[\{Co_2(L)(AcO)\}_2(O_2)][ClO_4]_2\cdot 4CH_3CN$ oxy-**3**, is isomorphous with oxy-**1**: the peroxo O(1)–O(2) bond distance is 1.415(4) Å and the Co(1) · · · Co(3) intermetallic separation is 4.3527(8) Å. Within the CoM(NCS) complexes **4**–**6**, **4** shows reversible oxygenation at −30 °C, whereas irreversible oxidation is observed for **5** and **6**.

Introduction

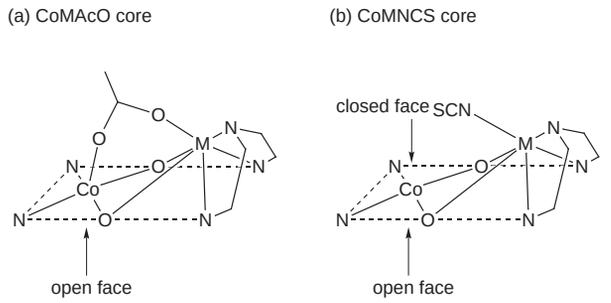
Dioxygen binding and activation on dinuclear metal complexes are of current interest relating to the physiological metabolism of dioxygen at bimetallic biosites.[1–5] Oxygenation of homodinuclear metal complexes like Cu^ICu^I[4] and $Fe^{II}Fe^{II}$[5] have been extensively studied with the aim of providing models for hemocyanin and hemerythrin, but less attention has been paid to oxygenation of heterodinuclear complexes.[6–9] It is well known that dioxygen reduction in cytochrome c oxidase is promoted by a CuFe pair in close proximity,[10,11] and this has stimulated studies of the oxygenation behaviour of heterodinuclear complexes having different combinations of metal ions. Recently some CuFe and CoCu complexes have been prepared and their oxygenation behaviour examined,[8,9] but such studies are still limited because of the difficulty in preparing suitable heterodinuclear core complexes.

The phenol-based compartmental ligand L^{2-}, having a "salen"-like N_2O_2 metal-binding site and a "saldien"-like N_3O_2 site sharing the phenolic oxygen, was developed in our laboratory for the study of heterodinuclear complexes (H_2salen = *N*,*N*′-bis(salicylidene)ethylenediamine; H_2saldien = *N*,*N*″-bis(salicylidene)diethylenetriamine).[12–21] Since [Co(salen)] is well known for its reactivity toward dioxygen,[22,23] the dinuclear Co^{II}-M^{II} complexes with Co^{II} in the "salen"-like site of the macrocycle are of great interest for studying oxygenation at the "Co(salen)" center with respect to the participation of the adjacent metal(II) ion.



Previously we reported the synthesis and the structures of the $Co^{II}M^{II}$ complexes $[CoM(L)(AcO)]ClO_4$ (M = Mn **1**, Fe **2** or Co **3**) and $[CoM(L)(NCS)]ClO_4$ (M = Mn **4**, Fe **5** or Co **6**).[16] They have a di(μ-phenoxo) $Co^{II}M^{II}$ core with the Co^{II} in the "salen" site and the M^{II} in the "saldien" site. The M^{II} in the "saldien" site largely deviates from the mean molecular plane, leaving the "closed" and the "open" faces for dioxygen. In complexes **1**–**3** an acetate group is involved in an additional bridge at the closed face (Scheme 1, (a)), leaving only the open face of "Co(salen)" for oxygenation. Complexes **4**–**6** assume a chain structure extended by a thiocyanate bridge in the solid but a discrete dinuclear core structure with isothiocyanato donation to the M^{II} in solution. Thus, both the closed and open faces of "Co(salen)" are available for oxygenation of **4**–**6** (Scheme 1, (b)). The oxygenation behaviour of **1**–**6** has now been studied in dmf by means of visible and EPR methods and discussed in view of the dinuclear core structure and the participation of the neighboring metal(II) ion. A part of this work was briefly reported previously.[19]

† *Supplementary data available*: ORTEP drawing of part of oxy-**3**, electronic spectra of **1**–**5**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/2197/, otherwise available from BLDSC (No. SUP 57560, 9 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).



Scheme 1 Possible oxygenation sites of CoM(AcO) **1**–**3** and CoM(NCS) **4**–**6** complexes.

Experimental

Measurements

Elemental analyses of C, H and N were obtained from the Service Center of Elemental Analysis at Kyushu University. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer using KBr discs, electronic spectra in dmf or acetonitrile ($\approx 1 \times 10^{-3}$ M) on Shimadzu MPS-2000 and UV-3100 spectrophotometers and X-band EPR spectra on a JEOL JEX-FE3X spectrometer at liquid nitrogen temperature.

Preparation

The complexes $[CoM(L)(AcO)]ClO_4$ (M = Mn **1**, Fe **2** or Co **3**) and $[CoM(L)(NCS)]ClO_4$ (M = Mn **4**, Fe **5** or Co **6**) were prepared by methods in our previous paper.[16]

Oxygenation studies

A dmf solution of a $Co^{II}M^{II}$ complex was prepared in a nitrogen or argon atmosphere and the reactivity towards dioxygen examined by means of electronic and EPR spectroscopy. The oxygenated complexes of **1** and **3**, $[\{CoMn(L)(AcO)\}_2(O_2)][ClO_4]_2 \cdot 4CH_3CN$ (oxy-**1**) and $[\{Co_2(L)(AcO)\}_2(O_2)][ClO_4]_2 \cdot 4CH_3CN$ (oxy-**3**), were isolated as good crystals when each oxygenated solution in acetonitrile was diffused with diethyl ether at −30 °C. Found: C, 41.83; H, 4.39; N, 9.37. Calc. for $C_{26}H_{34}ClCoMnN_5O_{11}$ oxy-**1**: C, 42.09; H, 4.62; N, 9.44. Found: C, 42.38; H, 4.35; N, 9.49. Calc. for $C_{52}H_{66}Cl_2Co_4N_{10}O_{21}$ oxy-**3**: C, 42.38; H, 4.51; N, 9.50%.

The oxidized complex of **6**, $[Co_2(L)(NCS)(OH)]ClO_4 \cdot 1.5H_2O$ **6′**, was obtained as brown crystals when an oxygenated dmf solution of **6** in the presence of an excess of $NaClO_4$ was diffused with 2-propanol at −30 °C. Calc. for $C_{25}H_{31}ClCo_2N_6O_{8.5}S$: C, 40.75; H, 4.24; N, 11.40. Found: C, 40.69; H, 4.29; N, 11.55%.

X-Ray crystallography

Single crystals of complexes oxy-**1** and oxy-**3** were picked up on a hand-made cold copper plate mounted inside a liquid N_2 Dewar vessel and mounted on a glass rod at −80 °C. Measurements were made on a Rigaku RAXIS-IV imaging plate area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) at −80 °C. Crystal-to-detector distance was 120 mm. In order to determine the cell constants and the orientation matrix, three oscillation photographs were taken with oscillation angle 2° and exposure time of 8 min for oxy-**1** and 6 min for oxy-**3** for each frame. The accurate unit-cell parameters used for the refinement were determined by least-squares calculations on the setting angles for 25 reflections with $2\theta = 22.08$–24.76° for oxy-**1** and 25.20–29.17° for oxy-**3** collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. Intensity data were collected by taking oscillation photographs (total oscillation range 162°, 54 frames, oscillation angle 3°, and exposure time 18 min for oxy-**1**, 165°, 55 frames, 3°, and 10 min for oxy-**3**). The data were corrected for Lorentz-polarization effects, but not for absorption. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 3.00\sigma(I)$). Crystal data and details of the structure determinations are summarized in Table 1.

CCDC reference number 186/1470.

See http://www.rsc.org/suppdata/dt/1999/2197/ for crystallographic files in .cif format.

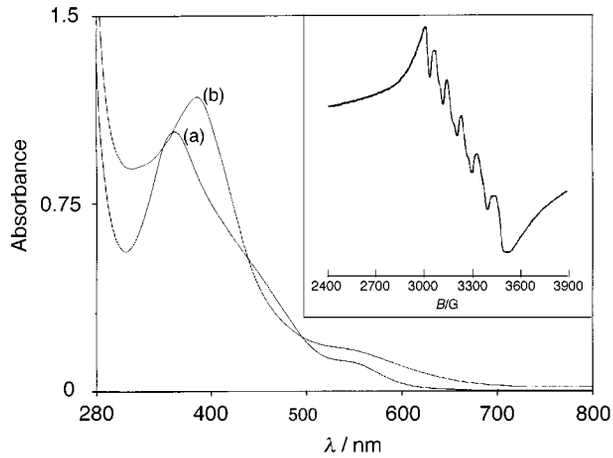


Fig. 1 Electronic spectra for complex **1** in dmf: (a) in the absence of O_2. (b) oxygenated at 0 °C. Insert: EPR spectrum of the oxygenated species in dmf at liquid nitrogen temperature.

Results and discussion

$[CoMn(L)(AcO)]ClO_4$ 1 and $[Co_2(L)(AcO)]ClO_4$ 3

These complexes have similar oxygenation behaviours. Introduction of dioxygen into a dmf solution of **1** at 0 °C caused an immediate change from red to dark red, suggesting formation of an oxygenated complex. Complex **1** shows an intense absorption band at 362 nm (ε 10500 M^{-1} cm^{-1}) and weaker bands near 460 (shoulder) and 560 nm (ε 990 M^{-1} cm^{-1}) (Fig. 1a) whereas its oxygenated complex shows an intense band at 382 nm (ε 11750 M^{-1} cm^{-1}) and an enhanced band at 550 nm (ε 1700 M^{-1} cm^{-1}) (Fig. 1b). The latter band of moderate intensity is characteristic of cobalt–dioxygen complexes and can be attributed to a LMCT band.[22–24] The oxygenated complex was stable at 0 °C for several days. When the oxygenated solution was purged with argon the original red solution was recovered. The reversible oxygenation/deoxygenation cycle for **1** is confirmed by observing the electronic spectral interconversion between traces a and b (Fig. 1). A similar reversible oxygenation/deoxygenation has been established for **3** at 0 °C (UV-vis: **3**, 365 (ε 10000), 480 (shoulder) and 565 nm (ε 1100); oxygenated complex of **3**, 392 (ε 11200) and 560 nm (ε 1500 M^{-1} cm^{-1})).[19]

In order to characterize the oxygenated complex in solution, EPR spectra of the oxygenated solution of **1** were studied (Fig. 1, insert). The observed isotropic EPR signal near $g \approx 2.0$ has a well resolved six-line hyperfine structure attributable to isolated Mn^{II} ($A_{iso} = 90$ G). This result demonstrates that the oxygenated complex is a peroxo dimer having the $Mn^{II}Co^{III}$–O–O–$Co^{III}Mn^{II}$ linkage. This was demonstrated by X-ray crystallography for $[\{CoMn(L)(AcO)\}_2(O_2)][ClO_4]_2 \cdot 4CH_3CN$ (oxy-**1**) and $[\{Co_2(L)(AcO)\}_2(O_2)][ClO_4]_2 \cdot 4CH_3CN$ (oxy-**3**) isolated from the oxygenated solutions of **1** and **3**, respectively.

An ORTEP[25] drawing of the cationic part of $[\{CoMn(L)(AcO)\}_2(O_2)][ClO_4]_2 \cdot 4CH_3CN$ oxy-**1** with 30% probability thermal ellipsoids is shown in Fig. 2 together with the atom-numbering scheme and the framework of the complex. Relevant bond distances and angles are given in Table 2. The cation

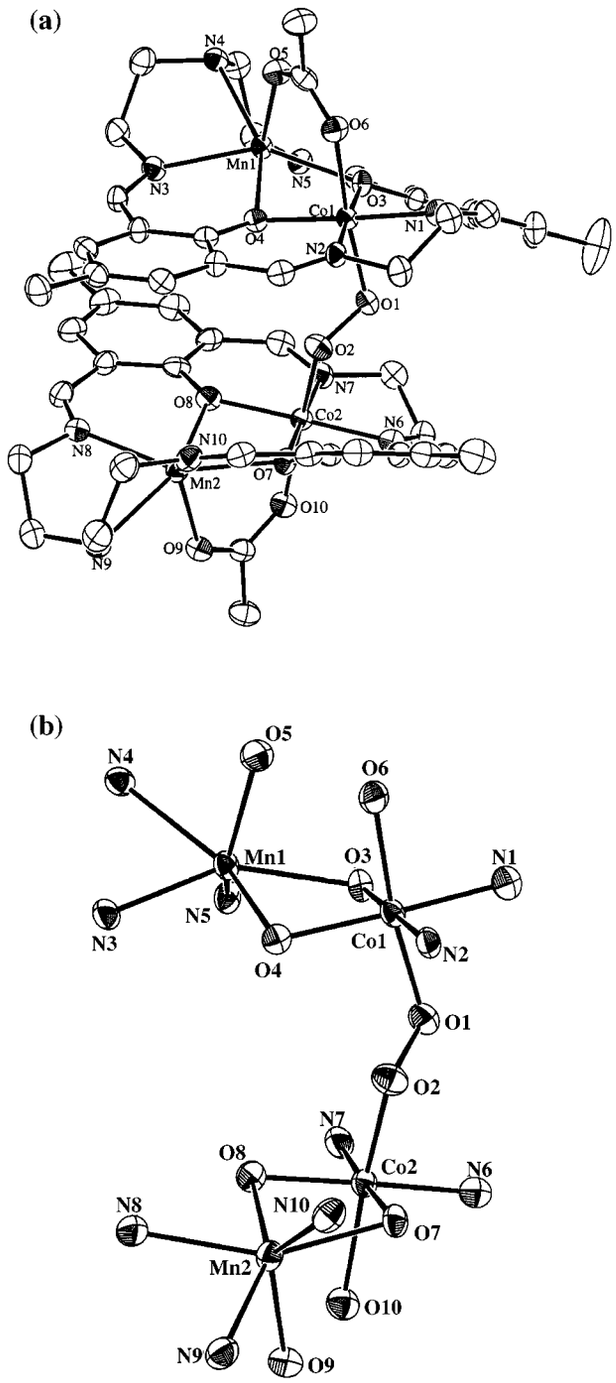


Fig. 2 (a) An ORTEP drawing of the $[\{CoMn(L)(AcO)\}_2(O_2)]^{2+}$ part of oxy-**1** with the atom numbering scheme. (b) The framework of oxy-**1**.

consists of two {CoMn(L)(AcO)} entities and a peroxo group; four acetonitrile molecules and two perchlorate ions are free from co-ordination and captured in the lattice. The {CoMn(L)(AcO)} part is very similar to the di(μ-phenoxo)-(μ-acetato) CoMn core of **1**,[16] having the Co in the "salen" site and the Mn in the "saldien" site. The acetate group bridges the metal ions at the closed face. Oxygenation occurs at the open face of "Co(salen)", *trans* to the bridging acetate oxygen, forming a μ-η^1:η^1 peroxo dimer with a Mn(1)Co(1)–O(1)–O(2)–Co(2)Mn(2) linkage; the Co(1)···Co(2) intermetallic separation is 4.359(1) Å. The two {CoMn(L)(AcO)} parts in oxy-**1** are not equivalent; the Co(1)···Mn(1) and Co(2)···Mn(2) intermetallic separations are 3.124(1) and 3.123(1) Å, respectively.

The peroxo O(1)–O(2) bond distance is 1.416(5) Å that is long relative to those of $[\{Co(salen)(dmf)\}_2(O_2)]$ (1.339(6) Å)[22e,26] and $[\{Co(salen)(pip)\}_2(O_2)]$ (1.383(7) Å; pip = piperidine).[22e,27] Instead, the Co(1)–O(1) and Co(2)–O(2) bond distances (1.866(4) and 1.849(4) Å, respectively) are shortened relative to those of the Co(salen) peroxo complexes (1.909(5)–

Table 1 Crystallographic data for $[\{CoM(L)(AcO)\}_2(O_2)][ClO_4]_2\cdot 4CH_3CN$ (M = Mn, oxy-**1**; Co, oxy-**3**)

	oxy-**1**	oxy-**3**
Formula	$C_{60}H_{72}Cl_2Co_2Mn_2N_{14}O_{18}$	$C_{60}H_{72}Cl_2Co_4N_{14}O_{18}$
M	1575.96	1583.95
Crystal size/mm	0.20 × 0.10 × 0.10	0.50 × 0.25 × 0.15
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	15.296(4)	14.833(2)
b/Å	17.578(5)	17.962(2)
c/Å	14.224(3)	13.820(3)
α/°	99.57(2)	98.656(9)
β/°	113.00(2)	110.540(8)
γ/°	80.14(2)	82.378(9)
U/Å^3	3447(1)	3395.9(7)
Z	2	2
D_c/g cm^{-3}	1.518	1.549
μ/cm^{-1}	9.87	11.19
No. reflections	10375	11147
No of data used ($I > 3.00\sigma(I)$)	7271	9158
No. variables	884	884
R	0.051	0.058
R'	0.066	0.083

Table 2 Selected bond distances (Å) and angles (°) of $[\{CoMn(L)(AcO)\}_2(O_2)][ClO_4]_2\cdot 4CH_3CN$ oxy-**1**

Co(1)–O(1)	1.866(4)	Co(1)–O(3)	1.916(4)
Co(1)–O(4)	1.918(4)	Co(1)–O(6)	2.003(4)
Co(1)–N(1)	1.881(5)	Co(1)–N(2)	1.872(4)
Co(2)–O(2)	1.849(4)	Co(2)–O(7)	1.931(4)
Co(2)–O(8)	1.921(4)	Co(2)–O(10)	2.046(4)
Co(2)–N(6)	1.875(5)	Co(2)–N(7)	1.866(4)
Mn(1)–O(3)	2.189(4)	Mn(1)–O(4)	2.243(3)
Mn(1)–O(5)	2.119(4)	Mn(1)–N(3)	2.222(5)
Mn(1)–N(4)	2.379(4)	Mn(1)–N(5)	2.223(4)
Mn(2)–O(7)	2.195(4)	Mn(2)–O(8)	2.233(3)
Mn(2)–O(9)	2.109(4)	Mn(2)–N(8)	2.223(5)
Mn(2)–N(9)	2.385(5)	Mn(2)–N(10)	2.207(5)
O(1)–Co(1)–O(3)	89.0(2)	O(1)–Co(1)–O(4)	96.2(2)
O(1)–Co(1)–O(6)	173.0(2)	O(1)–Co(1)–N(1)	85.8(2)
O(1)–Co(1)–N(2)	88.7(2)	O(3)–Co(1)–O(4)	85.6(1)
O(3)–Co(1)–O(6)	94.2(1)	O(3)–Co(1)–N(1)	92.9(2)
O(3)–Co(1)–N(2)	177.2(2)	O(4)–Co(1)–O(6)	90.3(2)
O(4)–Co(1)–N(1)	177.6(2)	O(4)–Co(1)–N(2)	96.3(2)
O(6)–Co(1)–N(1)	87.9(2)	O(6)–Co(1)–N(2)	87.8(2)
N(1)–Co(1)–N(2)	85.3(2)	O(2)–Co(2)–O(7)	81.2(2)
O(2)–Co(2)–O(8)	90.9(2)	O(2)–Co(2)–O(10)	172.8(2)
O(2)–Co(2)–N(6)	90.2(2)	O(2)–Co(2)–N(7)	96.0(2)
O(7)–Co(2)–O(8)	86.6(1)	O(7)–Co(2)–O(10)	91.8(1)
O(7)–Co(2)–N(6)	92.8(2)	O(7)–Co(2)–N(7)	176.6(2)
O(8)–Co(2)–O(10)	90.3(2)	O(8)–Co(2)–N(6)	178.6(2)
O(8)–Co(2)–N(7)	95.4(2)	O(10)–Co(2)–N(6)	88.4(2)
O(10)–Co(2)–N(7)	91.0(2)	N(6)–Co(2)–N(7)	85.3(2)
O(3)–Mn(1)–O(4)	72.0(1)	O(3)–Mn(1)–O(5)	88.6(1)
O(3)–Mn(1)–N(3)	147.3(1)	O(3)–Mn(1)–N(4)	135.6(1)
O(3)–Mn(1)–N(5)	79.1(2)	O(4)–Mn(1)–O(5)	87.8(1)
O(4)–Mn(1)–N(3)	79.9(1)	O(4)–Mn(1)–N(4)	151.0(2)
O(4)–Mn(1)–N(5)	129.0(1)	O(5)–Mn(1)–N(3)	107.1(2)
O(5)–Mn(1)–N(4)	84.6(1)	O(5)–Mn(1)–N(5)	133.0(2)
N(3)–Mn(1)–N(4)	75.6(2)	N(3)–Mn(1)–N(5)	107.4(2)
N(4)–Mn(1)–N(5)	74.1(2)	O(7)–Mn(2)–O(8)	73.3(1)
O(7)–Mn(2)–O(9)	84.3(1)	O(7)–Mn(2)–N(8)	151.3(2)
O(7)–Mn(2)–N(9)	132.7(2)	O(7)–Mn(2)–N(10)	79.1(2)
O(8)–Mn(2)–O(9)	89.1(1)	O(8)–Mn(2)–N(8)	81.0(2)
O(8)–Mn(2)–N(9)	152.9(2)	O(8)–Mn(2)–N(10)	125.9(1)
O(9)–Mn(2)–N(8)	108.2(2)	O(9)–Mn(2)–N(9)	86.8(2)
O(9)–Mn(2)–N(10)	133.4(2)	N(8)–Mn(2)–N(9)	75.0(2)
N(8)–Mn(2)–N(10)	107.0(2)	N(9)–Mn(2)–N(10)	74.0(2)
Co(1)–O(3)–Mn(1)	98.8(2)	Co(1)–O(4)–Mn(1)	97.0(1)
Co(2)–O(7)–Mn(2)	98.2(2)	Co(2)–O(8)–Mn(2)	97.2(2)

Table 3 Selected bond distances (Å) and angles (°) of $[\{Co_2(L)(AcO)\}_2(O_2)][ClO_4]_2\cdot 4CH_3CN$ oxy-**3**

Co(1)–O(1)	1.878(3)	Co(1)–O(3)	1.895(3)
Co(1)–O(4)	1.895(3)	Co(1)–O(6)	2.002(4)
Co(1)–N(1)	1.866(4)	Co(1)–N(2)	1.856(4)
Co(2)–O(3)	2.168(3)	Co(2)–O(4)	2.174(3)
Co(2)–O(5)	2.056(3)	Co(2)–N(3)	2.074(4)
Co(2)–N(4)	2.297(4)	Co(2)–N(5)	2.111(4)
Co(3)–O(2)	1.854(3)	Co(3)–O(7)	1.913(3)
Co(3)–O(8)	1.917(3)	Co(3)–O(10)	2.003(3)
Co(3)–N(6)	1.870(4)	Co(3)–N(7)	1.854(4)
Co(4)–O(7)	2.161(3)	Co(4)–O(8)	2.148(3)
Co(4)–O(9)	2.053(3)	Co(4)–N(8)	2.100(4)
Co(4)–N(9)	2.281(4)	Co(4)–N(10)	2.104(4)
O(1)–Co(1)–O(3)	90.5(1)	O(1)–Co(1)–O(4)	95.7(1)
O(1)–Co(1)–O(6)	173.3(1)	O(1)–Co(1)–N(1)	85.8(2)
O(1)–Co(1)–N(2)	88.0(2)	O(3)–Co(1)–O(4)	84.0(1)
O(3)–Co(1)–O(6)	92.8(1)	O(3)–Co(1)–N(1)	93.1(1)
O(3)–Co(1)–N(2)	178.0(2)	O(4)–Co(1)–O(6)	90.4(1)
O(4)–Co(1)–N(1)	176.8(1)	O(4)–Co(1)–N(2)	97.5(1)
O(6)–Co(1)–N(1)	88.2(2)	O(6)–Co(1)–N(2)	88.6(1)
N(1)–Co(1)–N(2)	85.4(2)	O(3)–Co(2)–O(4)	71.5(1)
O(3)–Co(2)–O(5)	85.9(1)	O(3)–Co(2)–N(3)	153.8(1)
O(3)–Co(2)–N(4)	128.4(1)	O(3)–Co(2)–N(5)	80.3(1)
O(4)–Co(2)–O(5)	89.2(1)	O(4)–Co(2)–N(3)	83.9(1)
O(4)–Co(2)–N(4)	155.3(1)	O(4)–Co(2)–N(5)	127.0(1)
O(5)–Co(2)–N(3)	103.1(2)	O(5)–Co(2)–N(4)	79.1(1)
O(5)–Co(2)–N(5)	133.1(1)	N(3)–Co(2)–N(4)	77.8(1)
N(3)–Co(2)–N(5)	108.9(2)	N(4)–Co(2)–N(5)	75.3(1)
O(2)–Co(3)–O(7)	83.1(1)	O(2)–Co(3)–O(8)	90.6(1)
O(2)–Co(3)–O(10)	175.3(1)	O(2)–Co(3)–N(6)	91.1(2)
O(2)–Co(3)–N(7)	95.5(1)	O(7)–Co(3)–O(8)	85.4(1)
O(7)–Co(3)–O(10)	92.2(1)	O(7)–Co(3)–N(6)	92.5(2)
O(7)–Co(3)–N(7)	177.0(2)	O(8)–Co(3)–O(10)	89.2(1)
O(8)–Co(3)–N(6)	177.1(1)	O(8)–Co(3)–N(7)	97.2(2)
O(10)–Co(3)–N(6)	88.9(2)	O(10)–Co(3)–N(7)	89.2(1)
N(6)–Co(3)–N(7)	84.9(2)	O(7)–Co(4)–O(8)	74.2(1)
O(7)–Co(4)–O(9)	84.8(1)	O(7)–Co(4)–N(8)	158.8(1)
O(7)–Co(4)–N(9)	123.2(1)	O(7)–Co(4)–N(10)	80.5(1)
O(8)–Co(4)–O(9)	88.2(1)	O(8)–Co(4)–N(8)	84.9(1)
O(8)–Co(4)–N(9)	158.2(1)	O(8)–Co(4)–N(10)	124.3(1)
O(9)–Co(4)–N(8)	98.2(1)	O(9)–Co(4)–N(9)	81.1(1)
O(9)–Co(4)–N(10)	138.0(1)	N(8)–Co(4)–N(9)	77.9(1)
N(8)–Co(4)–N(10)	109.4(2)	N(9)–Co(4)–N(10)	74.8(2)
Co(1)–O(3)–Co(2)	99.5(1)	Co(1)–O(4)–Co(2)	99.3(1)
Co(3)–O(7)–Co(4)	98.0(1)	Co(3)–O(8)–Co(4)	98.3(1)

1.914(5) Å).[22e,26,27] This fact suggests that the axial acetate co-ordination is strong compared with dmf or pip co-ordination, affording a high affinity towards dioxygen for the Co^{II} in the "salen" site. The Co(1)–O(1)–O(2) and Co(2)–O(2)–O(1) angles are 109.1(3) and 116.3(3)°, respectively, typical for Co(salen) peroxo complexes.[22e,26,27] The Co(1), Co(2), O(1), and O(2) are not coplanar and the Co(1)–O(1)–O(2)–Co(2) torsion angle with respect to the O(1)–O(2) edge is 149.5(2)°.

In each {CoMn(L)(AcO)} unit the Co assumes a pseudo octahedral geometry with the N_2O_2 donor atoms of the macrocycle on the equatorial plane and the bridging acetate oxygen and the peroxo oxygen at the axial positions. The in-plane Co–N and Co–O bond distances fall in the range 1.866(4)–1.931(4) Å, slightly longer than those of **1** (1.864(6)–1.916(4) Å). The axial Co–O (acetate) bond distance in oxy-**1** (Co(1)–O(6) 2.003(4), Co(2)–O(10) 2.046(4) Å), on the other hand, is considerably short relative to that of **1** (2.129(4) Å). The $\{CoN_2O_2\}$ part forms a good coplane; the sum of the bite angles about the Co is 360.1° (mean value for the two units). The O (acetate)–Co–O (peroxo) angle is 172.9° (mean).

The Mn in the "saldien" site is not involved in the oxygenation and retains a distorted trigonal-prismatic geometry as found for complex **1**, but some geometric changes occur upon oxygenation. The Mn–O (phenolate) and Mn–N (imine) bond distances of oxy-**1** (2.189(4)–2.243(3) Å) are slightly shortened relative to the corresponding bond distances of **1** (2.221(5)–2.258(4) Å). The Mn–N (amine) bond distances of oxy-**1** (Mn(1)–N(4) 2.379(4); Mn(2)–N(9) 2.385(4) Å) are also shortened relative to that of **1** (2.407(5) Å). Instead, the Mn–O (acetate) bond distances (Mn(1)–O(5) 2.119(4); Mn(2)–O(9) 2.109(4) Å) are slightly elongated relative to that of **1** (2.099(4) Å).

Table 4 Structural parameters of $[\{CoM(L)(AcO)\}_2(O_2)][ClO_4]_2\cdot 4CH_3CN$ (M = Mn, oxy-**1**; Co, oxy-**3**)

	oxy-**1**	oxy-**3**
O(1)–O(2)/Å	1.416(5)	1.415(4)
Co–O(1)–O(2)/°	109.1(3)	110.0(2)
Co–O(2)–O(1)/°	116.3(3)	117.0(2)
Co–O(1)–O(2)–Co/°	149.5(2)	143.7(2)
Co(1) ··· M(1) (unit 1)/Å	3.124(1)	3.105(8)
(unit 2)/Å	3.123(1)	3.0785(8)
Co(1) ··· Co(2) (unit 1–unit 2)/Å	4.359(1)	4.3527(8)
Co(1) ··· M(2) (unit 1–unit 2)/Å	6.143(1)	6.0776(8)
Co(2) ··· M(1) (unit 1–unit 2)/Å	5.617(1)	5.5295(9)
M(1) ··· M(2) (unit 1–unit 2)/Å	7.160(1)	7.0428(1)
d(Co)[a]/Å	0	0
d(M)[b]/Å (unit 1)	0.70	0.61
(unit 2)	0.69	0.57
τ[c]/° (unit 1)	9.30	12.27
(unit 2)	11.37	14.52
φ[d]/° (unit 1)	27.21	34.14
(unit 2)	31.41	31.81

[a] Deviation from the least-squares plane defined by the basal donor atoms at the "salen" site. [b] Deviation from the least-squares plane defined by the basal donor atoms at the "saldien" site. [c] The bending at O (phenolate)–O (phenolate) edge between the plane defined by the basal donor atoms at the "salen" site and the plane defined by the basal donor atoms at the "saldien" site. [d] Dihedral angle between the two aromatic rings.

The least-squares plane of the "salen" site and that defined by the two phenolic oxygens and two iminic nitrogens of the "saldien" site are bent at the O(3)–O(4) (O(7)–O(8)) edge. The dihedral angle between the two least-squares planes is 10.3° (mean for the two units) which is large compared with 4.6° for **1**. The {CoMn(L)(AcO)} unit also shows a distortion with respect to the Co–Mn edge, affording a saddle-like shape for the molecule. The dihedral angle between the two aromatic rings is 29.3° (mean) that is slightly smaller than the corresponding dihedral angle for **1** (31.3°).

Complex oxy-**3** (M = Co) is isomorphous with oxy-**1**.[19] Relevant bond distances and angles are given in Table 3. Some geometrical features for oxy-**1** and oxy-**3** are summarized in Table 4. The peroxo O(1)–O(2) bond distance (1.415(4) Å), the Co(1)–O(1)–O(2), Co(3)–O(2)–O(1) angles (110.0(2) and 117.0(2)°, respectively), and the Co(1) ··· Co(3) intermetallic separation (4.3527(8) Å) for oxy-**3** are comparable to the respective values for oxy-**1**. The Co(1)–O(1)–O(2)–Co(3) torsion angle of oxy-**3** (143.7(2)°) is smaller than that of oxy-**1** (149.5(2)°). The "Mn(saldien)" part of oxy-**1** and the "Co(saldien)" part of oxy-**3** differ from each other because of the different ionic radii of Mn^{II} and Co^{II}. The Mn-to-ligand bond distances in the former (2.217 Å, mean) are evidently longer than the Co-to-ligand bond distances in the latter (2.130 Å, mean). The distortions in the {CoM(L)(AcO)} core with respect to the O (phenolate)–O (phenolate) edge (τ) and the Co–M edge (φ) are both larger in oxy-**3**.

The above X-ray crystallographic studies indicate that the acetate bridge is retained in the oxygenation process to allow oxygenation at the open face of "Co(salen)". The initial oxygenation product must be the superoxo complex $[Co^{III}M^{II}(L)(AcO)(O_2^-)]^+$ that then reacts with another $Co^{II}M^{II}$ complex (**1** or **3**) to form the peroxo dimer (oxy-**1** or oxy-**3**); eqns. (1) and (2).

$$[Co^{II}M^{II}(L)(AcO)]^+ + O_2 \rightleftharpoons [Co^{III}M^{II}(L)(AcO)(O_2^-)]^+ \quad (1)$$

$$[Co^{II}M^{II}(L)(AcO)]^+ + [Co^{III}M^{II}(L)(AcO)(O_2^-)]^+ \rightleftharpoons [\{Co^{III}M^{II}(L)(AcO)\}_2(O_2^{2-})]^{2+} \quad (2)$$

Such a stepwise formation of a peroxo dimer through a superoxo complex has been demonstrated for Co(salen) and related Schiff base complexes.[22,23] It must be noted that Co(salen) itself predominantly forms the superoxo complex [Co(salen)(O_2^-)] in dmf[22,23] whereas **1** and **3** form the peroxo dimer. The X-ray crystallographic results for oxy-**1** and oxy-**3** indicate that the peroxo O–O bond is elongated whereas the Co–O (peroxo) bond is shortened relative to the corresponding bonds of the Co(salen) peroxo complexes. As discussed above the axial acetate oxygen is a strong enough donor to cause an efficient electron transfer from the Co^{II} to dioxygen in oxy-**1** and oxy-**3**. Such axial ligation of an acetate group is difficult for mononuclear Co(salen) and analogs. Thus, the M^{II} in the "saldien" site contributes to the axial acetate ligation to the "Co(salen)" through the acetate bridge formation.

When a solution of complex oxy-**1** was warmed to room temperature the spectrum changed with the decrease of the absorption bands at 382 and 550 nm, forming a yellow solution within 2 h, probably due to decomposition of oxy-**1**. Similarly the solution of oxy-**3** faded within 2 h when warmed to room temperature.

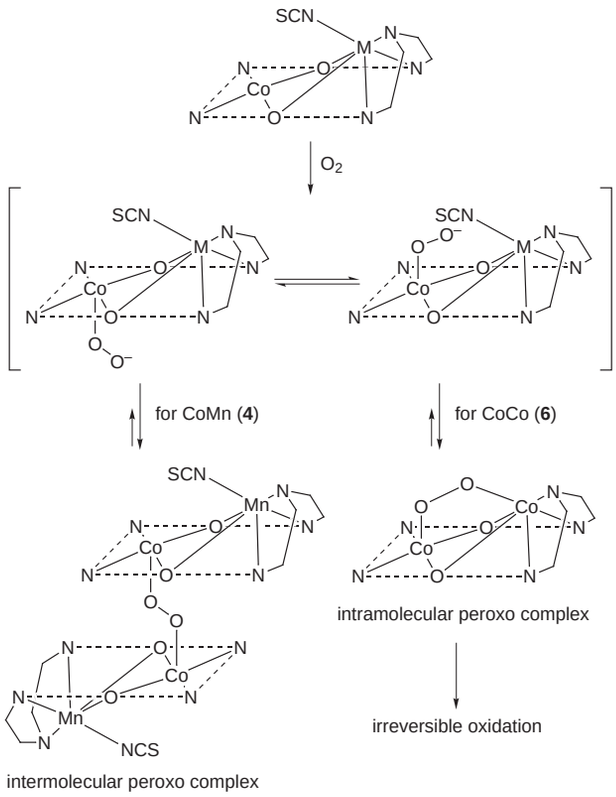
[CoFe(L)(AcO)]ClO_4 2

This complex was very sensitive toward molecular dioxygen so as to be oxidized even at −30 °C with a change from red to yellow. Complex **2** shows an intense absorption band at 358 nm (ε 10900 M^{-1} cm^{-1}) and weaker bands near 460 (shoulder) and 560 nm (ε 1400 M^{-1} cm^{-1}), whereas its oxidized yellow solution shows an intense band at 385 nm (ε 11200 M^{-1} cm^{-1}) but no distinct absorption in the visible region. The resulting yellow solution showed EPR signals at $g = 4.26$ and 2.01 that are attributable to isolated high-spin Fe^{III} (in frozen solution at liquid nitrogen). This result indicates that a $Co^{III}Fe^{III}$ species is formed. The mechanism for the conversion of **2** into the Co^{III}-Fe^{III} complex is not straightforward because the facile oxidation of Fe^{II} in the "saldien" site is recognized for analogous [Cu^{II}-Fe^{II}(L)]$^{2+}$ and [$Ni^{II}Fe^{II}$(L)]$^{2+}$ complexes.[13,14]

[CoMn(L)(NCS)]ClO_4 4

Complex **4** in dmf formed a dioxygen adduct at −30 °C with a change from red to dark red. Purging to the oxygenated solution with argon at −30 °C resulted in the recovery of the original red colour of **4**. The reversible oxygenation/deoxygenation was confirmed by the interconversion of the electronic spectra of **4** and its dioxygen adduct. Complex **4** shows an intense absorption band at 370 (ε 11000 M^{-1} cm^{-1}) and a weaker band at 540 nm (ε 500 M^{-1} cm^{-1}). The oxygenated solution of **4** (oxy-**4**) has an intense absorption band at 377 nm (ε 11400 M^{-1} cm^{-1}) and a moderately intense band at 595 nm (ε 2700 M^{-1} cm^{-1}). The latter band in the visible region (LMCT band) is located at longer wavelength relative to the corresponding bands for oxy-**1** and oxy-**3** (*ca.* 560 nm). The red-shift of the peroxide-to-Co^{III} charge transfer band for oxy-**4** can be explained by no axial donation to "Co(salen)". That is, the cobalt d orbitals of oxy-**4** are low-lying relative to those of oxy-**1** and oxy-**3**. The EPR spectrum of the oxygenated solution of **4** (in frozen dmf solution) shows an isotropic signal with six-line hyperfine structure near $g \approx 2.0$ ($A_{iso} = 93$ G) typical of isolated Mn^{II} as observed for oxy-**1**. The EPR result is in harmony with the formulation $Mn^{II}Co^{III}$–O–O–$Co^{III}Mn^{II}$ for the oxygenated complex.

As mentioned in the Introduction, both the open and closed faces of the "Co(salen)" can be available for oxygenation of complex **4**. A peroxo dimer formed at the closed face of "Co(salen)" is ruled out because this would give rise to a severe steric repulsion between two {CoMn(L)(NCS)} entities. Thus, the oxygenation of **4** to form the peroxo dimer (oxy-**4**) occurs at the open face of "Co(salen)" as provided for oxy-**1** and oxy-**3** (see Scheme 2, left).



Scheme 2 A possible oxygenation mechanism for complexes **4** and **6**.

When the oxygenated solution of complex **4** was warmed to 0 °C the spectrum of the peroxo dimer changed with a decrease of the bands at 377 and 595 nm, forming a yellow solution due to decomposition of oxy-**4** as observed for oxy-**1** and oxy-**3**.

[CoFe(L)(NCS)]ClO_4 5

Complex **5** was very sensitive to dioxygen like **2** and instantaneously oxidized at −30 °C when exposed. The oxidized solution showed an absorption spectrum very similar to that of the oxidized solution of **2**. Further, it showed EPR signals ($g = 4.24$ and 2.01) very similar to those of **2**. Evidently both the Co^{II} and Fe^{II} are oxidized with dioxygen to form a $Co^{III}Fe^{III}$ species.

[Co_2(L)(NCS)]ClO_4 6

Complex **6** was also sensitive to dioxygen and irreversibly oxidized even at −30 °C within 20 min and the formation of a peroxo complex was not confirmed. Thus, **6** and **3** differ in oxygenation behaviour in spite of the same Co_2 pair. Fig. 3 shows the electronic spectral changes of **6** upon oxidation at −30 °C. The absorption spectrum of **6** has two bands near 360 and 550 nm which are replaced by one at 393 nm on oxidation. The facile oxidation of **6** even at −30 °C may proceed by a mechanism involving a neighbouring Co^{II} in the "saldien" site.

We have noticed that the lifetime of the oxygenated solution of **6** varies with the complex concentration; the higher the concentration the longer is the lifetime. This fact suggests that a peroxo dimer and superoxo complex exist in an equilibrium in solution and the superoxo complex as a minor species is associated with the high sensitivity of **6**.

As mentioned above the oxygenation can occur either at the open or the closed face of "Co(salen)". Oxygenation at the open face forms the peroxo dimer [{$Co^{III}Co^{II}$(L)(NCS)}$_2$-(O_2^{2-})]$^{2+}$ as a dominant species. If oxygenation occurs at the closed face of "Co(salen)" a superoxo complex [Co^{III}-Co^{II}(L)(NCS)(O_2^-)]$^+$ is formed because of steric reasons as

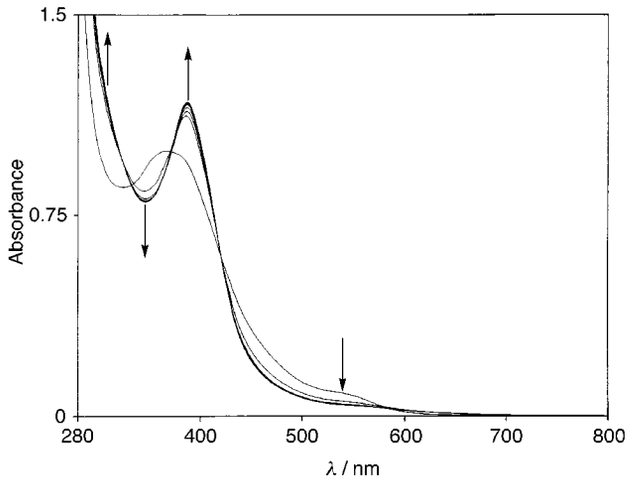


Fig. 3 Electronic spectral changes of complex **6** in dmf upon oxygenation at −30 °C.

discussed above. The terminal superoxo oxygen can make a bridge to the adjacent Co^{II} in the "saldien" site, by kicking out the thiocyanate ion, forming an intramolecular peroxo complex $[Co^{III}Co^{III}(L)(O_2^{2-})]^{2+}$ (see Scheme 2, right). The intramolecular peroxo complex must be formed as a minor species in the equilibrium, but **6** is oxidized to a $Co^{III}Co^{II}$ species through this complex at −30 °C. In our preliminary study the final product was shown to be the $Co^{III}Co^{II}$ complex $[Co_2(L)(NCS)(OH)]ClO_4 \cdot 1.5H_2O$ **6′**. It appears that the resulting "Co^{III}(saldien)" center may act as a strong oxidant of the oxidized complex **6** as in eqn. (3).

$$\{Co^{III}Co^{III}(L)\} + \{Co^{II}Co^{II}(L)\} \rightleftharpoons 2\{Co^{III}Co^{II}(L)\} \quad (3)$$

It must be noted that complexes **4** (CoMn) and **6** (Co_2) have essentially the same core structure but differ in oxygenation behaviour; **4** forms a stable peroxo dimer at −30 °C whereas **6** is oxidized at this temperature through an intramolecular peroxo intermediate. This can be explained by the participation of the adjacent metal in oxygenation. In the case of **4**, the adjacent Mn^{II} cannot be involved in two-electron reduction of dioxygen to form an intramolecular Co^{III}–O–O–Mn^{III} peroxo bond because of the preferred d^5 electronic configuration of Mn^{II}. In the case of **6**, the Co in the "saldien" site can be involved in such a two-electron reduction forming the intramolecular peroxo complex. Further, it should be noted that oxygenation of **3** significantly differs from that of **6** in spite of the same Co_2 pair. In the case of **3**, the formation of the peroxo bridge over the Co_2(AcO) core at the open face is difficult as judged from the core structure. Thus, the core structure bridged by an acetate group at the closed face suppresses a neighbouring effect of the adjacent metal(II) ion.

Conclusion

The $Co^{II}M^{II}$ complexes of the macrocyclic ligand L^{2-} show different oxygenation behaviours at the "Co(salen)" center, depending upon the dinuclear core structure and the nature of the M^{II} in the adjacent "saldien" site. Complexes $[CoMn(L)(AcO)]ClO_4$ **1** and $[Co_2(L)(AcO)]ClO_4$ **3** have an acetate-bridged core in solution leaving the open face of "Co(salen)" for oxygenation. The resulting peroxo dimers $[\{CoM(L)(AcO)\}_2(O_2)][ClO_4]_2$ (M = Mn, oxy-**1**; Co, oxy-**3**) were stable at 0 °C and deoxygenated by purging with argon at this temperature. The complexes $[CoFe(L)(AcO)]ClO_4$ **2** and $[CoFe(L)(NCS)]ClO_4$ **5** were immediately oxidized to $Co^{III}Fe^{III}$ species at −30 °C. The mechanism for the oxidation was complicated because the Fe^{II} in the "saldien" site is air-sensitive. Complex $[CoMn(L)(NCS)]ClO_4$ **4** showed reversible oxygenation at −30 °C forming the peroxo dimer $[\{CoMn(L)(NCS)\}_2(O_2)]^{2+}$, whereas $[Co_2(L)(NCS)]ClO_4$ **6** showed a high sensitivity toward dioxygen and was oxidized even at −30 °C. The marked sensitivity of **6** is explained by a participation of the adjacent Co^{II} in the oxidation; the Co^{II} in the "saldien" site can be involved in two-electron reduction of dioxygen to form an intramolecular peroxo intermediate $[Co_2(L)(O_2)]^{2+}$. Thus, the present study illustrates that the oxygenation of the "Co(salen)" center can be drastically changed not only by the metal ion in the "saldien" site but also by the stereochemistry of the core structure constructed by the exogenous anionic donor AcO^- or NCS^-.

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