oxy)prismane adducts with Mo(CO)$_3$ and on the oxidative decarbonylation of these compounds with quinones or alkyl peroxides.

Acknowledgment. The support of this work by a grant (GM-26671) from the National Institutes of Health is gratefully acknowledged.

Supplementary Material Available: Listings of positional and thermal parameters for $(Et_4N)_3[Fe_6S_6(p\text{-}OMePhO)_3]$ (I), $(Et_4N)_3\{Fe_6S_6(p\text{-}OMePhO)_6[Mo(CO)_3]_2\}$ (II), $(Et_4N)_3\{Fe_6S_6(p\text{-}MePhO)_6[W(CO)_3]_2\}$ (III), and $(Et_4N)_4\{Fe_6S_6(p\text{-}COMePhO)_6[Mo(CO)_3]_2\}$ (IV) (Tables S1–S4) (55 pages); listings of structure factors (Tables S5–S8) (57 pages). Ordering information is given on any current masthead page.

Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, FRG,
and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, FRG

Synthesis and Coordination Chemistry of the Hexadentate Ligands 1,4,7-Tris(2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^1) and 1,4,7-Tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^2). Crystal Structures of $[HL^1Cu^{II}]$ and $[L^2Fe^{III}]$acacH

Ulf Auerbach,[1a] Uwe Eckert,[1a] Karl Wieghardt,*,[1a] Bernhard Nuber,[1b] and Johannes Weiss[1b]

Received June 7, 1989

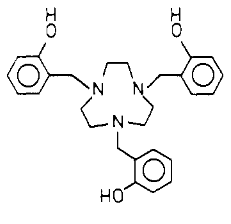
Two new hexadentate macrocycles containing phenolate pendant arms have been prepared from 1,4,7-triazacyclononane and 3 equiv of 2-(bromomethyl)phenyl acetate: 1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^1; $C_{27}H_{33}N_3O_3$) and 1,4,7-tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^2, $C_{39}H_{57}N_3O_3$). The reaction of trivalent first-row transition metals with the trianions affords monomeric pseudooctahedral complexes, of which the following have been characterized: L^1Mn^{III}; L^1Fe^{III}; L^2Co^{III}; $[L^2Fe^{III}]$acacH; L^2Fe^{III}; L^2Mn^{III}. The reaction of copper(II) perchlorate with the new ligands affords five-coordinate species: HL^1Cu^{II}; $[H_2L^2Cu^{II}]ClO_4$ (green), $[HL^2Cu^{II}]NaClO_4$ (red). $Co(BF_4)_2{\cdot}6H_2O$ reacts with H_3L^1 in the presence of air to give a trinuclear complex: $[(L^1Co^{III})_2Co^{II}](BF_4)_2{\cdot}H_2O$. The crystal structures of $[HL^1Cu^{II}]$ (**1**) and $[L^2Fe^{III}]$acacH (**2**), where acacH is acetylacetone, have been determined by X-ray crystallography: (**1**) space group $P2_1/n$, a = 8.687 (4) Å, b = 13.320 (9) Å, c = 20.789 (8) Å, β = 102.09 (4)°, Z = 4; (**2**) space group $P2_1/n$, a = 12.347 (9) Å, b = 18.929 (9) Å, c = 17.699 (9) Å, β = 92.23 (6)°, Z = 4. In **1** the Cu(II) center is in a square-based-pyramidal environment of three nitrogen donors and two phenolate oxygen atoms whereas the ferric ion in **2** is in a pseudooctahedral environment (N_3O_3 donor set). Electronic spectral data, magnetic properties, and the electrochemistry of the new complexes are reported.

Introduction

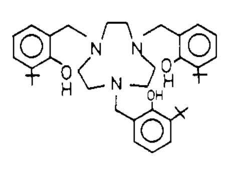
In recent years the tridentate, facially coordinating macrocycle 1,4,7-triazacyclononane has been repeatedly N-functionalized and a series of potentially hexadentate ligands have been synthesized and their coordination chemistry investigated.[2,3] Chart I summarizes these ligands. In this paper we present two new such ligands, which contain phenolate pendant arms. Recently, Moore and co-workers[4] have reported the first ligand of this kind, namely 1,4,7-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane, which was shown to form a stable gallium(III) complex. This work prompted us to publish our own results now. We had independently synthesized 1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^1) and 1,4,7-tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^2) and studied their coordination chemistry with first-row transition metals such as Fe(III), Mn(III), Co(III), and Cu(II).

Experimental Section

The ligand 1,4,7-triazacyclononane (tacn) was prepared according to published procedures.[5] All other chemicals were obtained from commercial sources and used as received.



H_3L^1



H_3L^2

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these should be handled behind suitable protective shields.

Synthesis of 1,4,7-Tris(2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^1). To a solution of dry, finely powdered KOH (3.90 g; 66 mmol) in toluene (30 mL) was added 1,4,7-triazacyclononane (1.29 g; 10 mmol). To this solution was added dropwise a toluene solution (20 mL) of 2-(bromomethyl)phenyl acetate[6] (6.87 g; 30 mmol) at 0 °C. The combined solutions were stirred at room temperature for 12 h. The precipitated KBr was filtered off, and the solvent was removed by evaporation under reduced pressure. To the resulting orange oil was added 0.1 M NaOH (100 mL), and the solution was stirred at 20 °C for 3 h, after which time the product was extracted from the aqueous phase with CH_2Cl_2 (three times with 50 mL). The combined organic phases were dried over $MgSO_4$. After removal of the solvent by rotary evaporation a colorless solid was obtained in 20–30% yield with respect to 1,4,7-triazacyclononane.

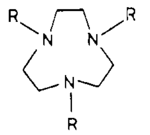
^{1}H NMR ($CDCl_3$; δ): 6.71–7.22 (m, 12 H, phenyl), 3.74 (s, 6 H, $N{-}CH_2{-}R$), 2.79 (s, 12 H, $N{-}CH_2CH_2{-}N$). The phenolic protons were not observed. ^{13}C NMR (20 °C, $CDCl_3$; δ): 157.3, 129.2, 129.1, 122.0, 119.4, 116.1, 62.6, 55.7. MS: m/z 447. UV-vis (CH_3CN; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 275 (2400), 280 (sh).

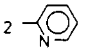
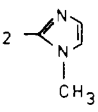
The colorless trisodium salt, Na_3L^1, was prepared from sodium methanolate and H_3L^1 (3:1) dissolved in dry methanol followed by rotary evaporation of the solvent under reduced pressure. UV-vis (CH_3CN;

---

(1) (a) Ruhr-Universität Bochum. (b) Universität Heidelberg.
(2) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.
(3) (a) Arishima, T.; Hamada, K.; Takamoto, S. *Nippon Kagaku Kaishi* **1973**, 1119. (b) Wieghardt, K.; Bossek, U.; Guttmann, M.; Weiss, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 81. (c) Sayer, B. A.; Michael, J. P.; Hancock, R. D. *Inorg. Chim. Acta* **1983**, *77*, L63. (d) Gahan, L. R.; Lawrence, G. A.; Sargeson, A. M. *Aust. J. Chem.* **1982**, *35*, 1119. (e) Polikarpov, M. Yu.; Shcherbakov, B. K.; Bel'skii, F. I.; Medved, T. Ya.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1669. (f) Christiansen, L.; Hendrickson, D. N.; Toftlund, H.; Wilson, S. R.; Xie, C. L. *Inorg. Chem.* **1986**, *25*, 2813. (g) Wieghardt, K.; Schöffmann, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877. (h) DiVaira, M.; Mani, F.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1989**, 126.
(4) Moore, D. A.; Fanwick, P. E.; Welch, M. J. *Inorg. Chem.* **1989**, *28*, 1504.
(5) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268.
(6) (a) Range, R. *Tetrahedron* **1971**, *27*, 1499. (b) Karlin, K. D.; Cohen, B. I.; Hayes, J. C.; Farooq, A.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 147.

Chart I. N-Functionalized 1,4,7-Triazacyclononane Ligands



R	ref
CH_2COOH	3a
CH_2SO_3H	3b
CH_2CH_2OH	3c
$CH_2CH_2NH_2$	3d
CH_2PO_3H	3e
CH_2 	3f,g
CH_2 	3h

λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 293 (3430).

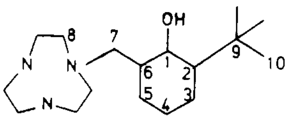
Synthesis of 1,4,7-Tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^2). 2-*tert*-Butyl-6-methylphenyl Acetate. To a mixture of 6-*tert*-butyl-*o*-cresol (20 g; 0.12 mol) and acetic anhydride (26 g, 0.24 mol) were added 5 drops of concentrated H_2SO_4, and this solution was heated to reflux for 12 h. The unreacted acetic anhydride was removed under reduced pressure, and the resulting crude oil was distilled. The fraction boiling at 75 °C (0.03 mmHg) was collected. Yield: 24 g, 95%.

2-(Bromomethyl)-6-*tert*-butylphenyl Acetate. To a solution of the above product (20 g; 97 mmol) in CCl_4 (100 mL) was added *N*-bromosuccinimide. In order to start the reaction, azobis(isobutyronitrile) (0.2 g) was added. The solution was heated to reflux until the reaction was initiated. After the reaction was completed succinimide was filtered off, and the solvent was removed under reduced pressure. The residual oil was distilled in vacuo. The fraction boiling at 90 °C (0.03 mmHg) was collected, which crystallized upon standing for 5 days at 0 °C: Yield: 23 g; 83%.

^{1}H NMR ($CDCl_3$ δ): 7.00–7.35 (m, 3 H), 4.35 (s, 2 H), 2.40 (s, 3 H), 1.35 (s, 9 H).

1,4,7-Tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L^2). To a suspension of 1,4,7-triazacyclononane (6.45 g; 50 mmol) and powdered KOH (19.5 g; 0.19 mol) in toluene (40 mL) was added with cooling (0 °C) a solution of 2-(bromomethyl)-6-*tert*-butylphenyl acetate (42.7 g; 0.15 mol) in toluene (40 mL). This solution was stirred at room temperature for 12 h, after which time a colorless precipitate (KBr) was filtered off, washed with toluene (20 mL), and discarded. The solvent from the combined filtrates was removed by evaporation under reduced pressure. The resulting red, viscous oil was dissolved in tetrahydrofuran (150 mL) and sodium methanolate (8.1 g; 0.15 mol), and water (10 mL) was added. This solution was vigorously stirred for 12 h. Within 1 h the red oil had completely dissolved, and after 12 h a colorless precipitate of the desired ligand H_3L^2 had formed, which was collected by filtration and dried in vacuo over KOH. Yield: 19.5 g; 60%.

^{1}H NMR ($CDCl_3$; δ): 6.65–7.2 (m, 9 H), 3.70 (s, 6 H), 2.75 (s, 12 H) 1.40 (27 H). The phenolic protons were not observed. ^{13}C NMR (20 °C, $CDCl_3$; δ): 156.3 (1), 136.7 (2), 122.4 (3), 118.6 (4), 126.4 (5), 127.1 (6), 63.1 (7), 55.5 (8), 29.5 (9), 34.6 (10). These ten signals were assigned as shown:



MS: *m/z* 615. UV–vis (λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): (CH_2Cl_2) 280 (6.4 × 10^3), 276 (sh); (CH_3CN/KOH) 312 (12.5 × 10^3).

Synthesis of Transition-Metal Complexes. L^1Mn^{III}. To an aqueous solution (20 mL) of $Mn(ClO_4)_2·6H_2O$ (0.18 g; 0.5 mmol) was added a solution of H_3L^1 (0.22 g; 0.5 mmol) dissolved in acetone (30 mL) at room temperature with stirring. In the presence of air the color changed to deep green and a green solid slowly precipitated, which was collected by filtration, washed with ethanol and ether, and air-dried. Yield: 0.16 g; 66%.

Anal. Calcd for $C_{27}H_{30}N_3O_3Mn$: C, 64.9; H, 6.1; N, 8.4; Mn, 11.0. Found: C, 64.7; H, 6.2; N, 8.2; Mn, 10.8.

L^1Fe^{III}. To a solution of $Fe(ClO_4)_3·9H_2O$ (0.26 g; 0.5 mmol) in an acetone/water mixture (2:1; 30 mL) was added an acetone solution (30 mL) of H_3L^1 (0.22 g; 0.5 mmol) at room temperature. From the resulting deep red solution a microcrystalline red solid slowly precipitated, which was collected by filtration. Yield: 0.18 g; 72%.

Anal. Calcd for $C_{27}H_{30}N_3O_3Fe$: C, 64.8; H, 6.0; N, 8.4; Fe, 11.3. Found: C, 64.6; H, 5.9; N, 7.9; Fe, 11.2.

$[(L^1Co^{III})_2Co^{II}](BF_4)_2·H_2O$. To a solution of H_3L^1 (0.22 g; 0.5 mmol) in acetone (30 mL) was added an acetone solution (10 mL) of $Co(BF_4)_2·6H_2O$ (0.26 g; 0.75 mmol). The solution was stirred at 50 °C in the presence of air for 1 h. A pink precipitate formed within 12 h at 20 °C, which was collected by filtration and recrystallized from boiling methanol. Yield: 0.72 g; 35%.

Anal. Calcd for $C_{54}H_{60}N_6O_6Co_3(BF_4)_2·H_2O$: C, 51.6; H, 5.0; N, 6.7; Co, 14.1. Found: C, 51.7; H, 5.0; N, 6.9; Co, 13.9.

$[HL^1Cu^{II}]$. To a mixture of H_3L^1 (0.09 g; 0.2 mmol) in dry methanol (30 mL) was added sodium (0.015–0.02 g). After the sodium had completely dissolved a solution of $Cu(ClO_4)_2·6H_2O$ (0.074 g; 0.2 mmol) in methanol (10 mL) was added. The mixture was stirred for 3 h at 20 °C until a clear deep green solution was obtained, which was allowed to stand for 2–3 days at 20 °C. Deep green crystals precipitated, which were filtered off and air-dried. Yield: 0.057 g; 54%.

Anal. Calcd for $C_{27}H_{31}N_3O_3Cu$: C, 63.70; H, 6.13; N, 8.25. Found: C, 63.3; H, 6.2; N, 8.1.

$[L^2Fe^{III}]$acacH. H_3L^2 (0.62 g; 1 mmol) and $Fe(acac)_3$ (0.35 g; 1 mmol), where acac is the monoanion acetylacetonate, dissolved in an acetone/water mixture (9:1; 100 mL) were heated to reflux for 4 h. The deep red, hot solution was filtered and allowed to stand at room temperature for 20 h, after which time red brown crystals suitable for X-ray crystallography had formed. These were collected by filtration. Yield: 0.65 g, 67%.

Anal. Calcd for $C_{39}H_{54}N_3O_3Fe·C_5H_8O_2$: C, 68.7; H, 8.3; N, 5.5. Found: C, 68.6; H, 8.5; N, 5.5.

$[L^2Fe^{III}]$. A mixture of H_3L^2 (0.31 g; 1 mmol), $Fe(ClO_4)_3·9H_2O$ (0.18 g; 0.5 mmol), and sodium methanolate (0.11 g; 2.0 mmol) in methanol (50 mL) was heated to reflux for 2 h. After filtration of the hot deep red solution water was added (100 mL), which initiated the precipitation of a red brown microcrystalline solid, which was collected by filtration and dried in vacuo. Yield: 0.31 g; 93%.

Anal. Calcd for $C_{39}H_{54}N_3O_3Fe$: C, 70.0; H, 8.1; N, 6.3. Found C, 68.9; H, 7.9; N, 6.1.

$[L^2Mn^{III}]$. A mixture of $Mn(ClO_4)_2·6H_2O$ (0.14 g; 0.5 mmol) and H_3L^2 (0.31 g; 0.5 mmol) in methanol (40 mL) was heated to reflux under an argon atmosphere for 4 h. The resulting solution was stirred at 20 °C in the presence of air for 12 h. A green solid precipitated upon addition of water (100 mL) from the then green solution. The solid was collected by filtration and dried in vacuo over KOH. Yield: 0.30 g; 90%.

Anal. Calcd for $C_{39}H_{54}N_3O_3Mn$: C, 70.1; H, 8.1; N, 6.3. Found: C, 70.3; H, 8.7; N, 6.5.

$[L^2Co^{III}]$. A mixture of $Co(acac)_2$ (0.085 g; 0.3 mmol) and H_3L^2 (0.185 g; 0.3 mmol) in acetone (40 mL) was heated to reflux for 4 h in the presence of air. The deep green solution was filtered and allowed to stand at 20 °C for 20 h, after which time green microcrystals had precipitated, which were collected by filtration. Yield: 0.18 g; 63%.

Anal. Calcd for $C_{39}H_{54}N_3O_3Co$: C, 69.7; H, 8.1; N, 6.2. Found: C, 69.7; H, 8.3; N, 6.1.

$[H_2L^2Cu^{II}]·ClO_4$ (Green). A mixture of $Cu(ClO_4)_2·6H_2O$ (0.11 g; 0.3 mmol) and H_3L^2 (0.185 g; 0.3 mmol) in methanol (50 mL) was heated to reflux for 30 min. After filtration of the hot red solution $NaClO_4$ (0.5 g) and a few drops of 1 M $HClO_4$ were added until a green solution was obtained. Upon standing at room temperature, the solution yielded green crystals, which were collected by filtration. Yield: 0.18 g; 75%.

Anal. Calcd for $C_{39}H_{56}N_3O_3CuClO_4$: C, 60.14; H, 7.25; N, 5.4. Found: C, 59.8; H, 7.4; N, 5.3.

$[HL^2Cu^{II}]NaClO_4$ (Red). It was found that by using the above procedure red crystals precipitated from the red solution when the reaction mixture was heated to reflux for 4 h without addition of $HClO_4$ but with addition of $NaClO_4$ (0.5 g). This material contains one sodium cation per copper ion. Yield: 0.09 g; 31%.

Anal. Calcd for $C_{39}H_{55}N_3O_3CuNaClO_4$: C, 58.49; H, 6.92; N, 5.25; Cl, 4.42; Cu, 7.93; Na, 2.87. Found: C, 58.9; H, 7.2; N, 5.2; Cl, 4.6; Cu, 8.4; Na, 3.1.

X-ray Diffraction Studies of $[HL^1Cu]$ (1) and $[L^2Fe]$acacH (2). Intensities and lattice parameters of a deep green irregularly shaped crystal of **1** and a brown-red tabular-shaped crystal of **2** were measured on a Syntex R3 diffractometer at ambient temperature. Crystal parameters and details of the data collection and refinement are given in Table I (for full details see Table S1 in the supplementary material). Empirical absorption corrections (ψ scans of six reflections with $6 < 2\theta < 35°$) were carried out in each case.[7] Both structures were solved by conventional Patterson and difference Fourier methods. The function minimized

---

[7] Computations were carried out on an ECLIPSE computer by using the program package SHELXTL (Sheldrick, G. M., Universität Göttingen, revision 3.0, 1981).

Table I. Crystallographic Data for HL^1Cu (**1**) and $[L^2Fe]acacH$ (**2**)

	1	**2**
formula	$C_{27}H_{31}N_3O_3Cu$	$C_{39}H_{54}N_3O_3Fe{\cdot}C_5H_8O_2$
fw	509.1	768.8
space group	$P2_1/n$	$P2_1/n$
a, Å	8.687 (4)	12.347 (9)
b, Å	13.320 (9)	18.929 (9)
c, Å	20.789 (8)	17.699 (9)
β, deg	102.09 (4)	92.23 (6)
V, Å^3	2352	4133
Z	4	4
T, °C	22	22
λ(Mo Kα), Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.44	1.15
μ, cm^{-1}	9.62	4.01
transm coeff	0.78–1.00	0.86–1.00
$R(F_o)^a$	0.046	0.064
$R_w(F_o)^b$	0.039	0.059

[a] $R(F_o) = \sum|\Delta F|/\sum|F_o|$. [b] $R_w(F_o) = [\sum w\Delta F^2/\sum|F_o|^2]^{1/2}$; $w = 1/\sigma^2(I)$.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **1**

atom	x	y	z	U^a
Cu(1)	883 (1)	6137 (1)	6994 (1)	29 (1)*
N(1)	−322 (3)	7688 (3)	7015 (1)	28 (1)*
N(2)	1597 (4)	6816 (3)	6202 (2)	33 (1)*
N(3)	2738 (3)	6874 (2)	7563 (2)	29 (1)*
C(1)	−481 (5)	8043 (3)	6339 (2)	36 (2)*
C(2)	961 (5)	7848 (3)	6063 (2)	37 (2)*
C(3)	3306 (5)	6819 (4)	6445 (2)	40 (2)*
C(4)	3711 (4)	7312 (4)	7121 (2)	40 (2)*
C(5)	2062 (5)	7665 (3)	7924 (2)	37 (2)*
C(6)	824 (4)	8308 (3)	7478 (2)	35 (2)*
C(7)	−1917 (4)	7660 (4)	7165 (2)	40 (2)*
O(1)	−2552 (4)	9223 (2)	7962 (2)	53 (1)*
C(8)	−1821 (5)	6546 (4)	8148 (2)	46 (2)*
C(9)	−2007 (5)	6391 (4)	8787 (2)	50 (2)*
C(10)	−2426 (5)	7181 (4)	9138 (2)	46 (2)*
C(11)	−2633 (5)	8120 (3)	8876 (2)	39 (2)*
C(12)	−2399 (4)	8288 (3)	8238 (2)	36 (2)*
C(13)	−2004 (5)	7499 (4)	7869 (2)	37 (2)*
C(14)	1122 (4)	6151 (4)	5621 (2)	43 (2)*
O(2)	−812 (3)	5420 (2)	6435 (1)	38 (1)*
C(15)	−1411 (6)	6477 (4)	4798 (2)	53 (2)*
C(16)	−3023 (6)	6488 (4)	4629 (2)	65 (2)*
C(17)	−3887 (5)	6127 (4)	5045 (2)	59 (2)*
C(18)	−3153 (5)	5751 (4)	5655 (2)	46 (2)*
C(19)	−1519 (5)	5752 (3)	5842 (2)	33 (1)*
C(20)	−630 (5)	6109 (4)	5399 (2)	37 (1)*
C(21)	3730 (4)	6156 (4)	8039 (2)	44 (2)*
O(3)	915 (3)	5057 (2)	7602 (1)	37 (1)*
C(22)	3442 (5)	5692 (4)	9169 (2)	52 (2)*
C(23)	2690 (6)	5212 (4)	9601 (2)	59 (2)*
C(24)	1334 (6)	4671 (4)	9355 (2)	53 (2)*
C(25)	743 (5)	4624 (3)	8684 (2)	40 (2)*
C(26)	1500 (4)	5118 (3)	8244 (2)	34 (1)*
C(27)	2878 (5)	5666 (3)	8492 (2)	37 (2)*
H	−3240 (44)	9552 (31)	8190 (18)	62

[a] Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **2**

atom	x	y	z	U^a
Fe(1)	2545 (1)	6509 (1)	9574 (1)	34 (1)*
O(1)	2032 (3)	7438 (2)	9410 (2)	44 (2)*
O(2)	1776 (3)	6091 (2)	8746 (2)	39 (2)*
O(3)	3895 (3)	6607 (2)	9116 (2)	41 (2)*
N(1)	1250 (4)	6389 (3)	10413 (3)	36 (2)*
N(2)	2842 (4)	5417 (3)	10013 (3)	35 (2)*
N(3)	3449 (4)	6709 (3)	10682 (3)	36 (2)*
C(1)	967 (5)	5627 (3)	10375 (4)	42 (3)*
C(2)	1946 (5)	5162 (4)	10486 (4)	45 (3)*
C(3)	3874 (5)	5455 (4)	10450 (4)	44 (3)*
C(4)	3878 (5)	6044 (3)	11028 (4)	46 (3)*
C(5)	2647 (5)	7049 (4)	11155 (4)	44 (3)*
C(6)	1615 (5)	6607 (4)	11185 (3)	44 (3)*
C(7)	296 (5)	6809 (3)	10146 (4)	42 (3)*
C(8)	2990 (5)	4938 (3)	9348 (4)	42 (3)*
C(9)	4327 (5)	7218 (4)	10551 (4)	45 (3)*
C(10)	1296 (5)	7864 (4)	9695 (4)	39 (2)
C(11)	471 (5)	7590 (4)	10119 (4)	41 (2)
C(12)	−241 (6)	8047 (4)	10466 (4)	51 (2)
C(13)	−112 (6)	8764 (4)	10388 (4)	64 (2)
C(14)	646 (6)	9031 (4)	9937 (4)	65 (2)
C(15)	1375 (6)	8610 (4)	9552 (4)	53 (2)
C(16)	2141 (6)	8888 (4)	8970 (4)	66 (2)
C(17)	1860 (7)	8563 (5)	8216 (4)	91 (3)
C(18)	3320 (6)	8751 (5)	9202 (5)	90 (3)
C(19)	2037 (8)	9692 (4)	8879 (6)	111 (4)
C(20)	1519 (5)	5451 (4)	8492 (4)	38 (2)
C(21)	2024 (5)	4849 (3)	8824 (3)	34 (2)
C(22)	1709 (5)	4180 (4)	8583 (4)	41 (2)
C(23)	911 (5)	4099 (4)	8044 (4)	52 (2)
C(24)	450 (6)	4673 (4)	7701 (4)	52 (2)
C(25)	739 (5)	5360 (4)	7896 (4)	43 (2)
C(26)	300 (6)	6010 (4)	7469 (4)	58 (2)
C(27)	1219 (7)	6416 (5)	7124 (4)	81 (3)
C(28)	−310 (7)	6500 (5)	7989 (5)	83 (3)
C(29)	−504 (7)	5791 (5)	6826 (5)	96 (3)
C(30)	4922 (5)	6734 (3)	9313 (4)	36 (2)
C(31)	5192 (5)	6975 (4)	10037 (4)	37 (2)
C(32)	6268 (5)	7070 (4)	10266 (4)	51 (2)
C(33)	7052 (6)	6935 (4)	9767 (4)	57 (2)
C(34)	6800 (6)	6724 (4)	9045 (4)	53 (2)
C(35)	5730 (5)	6637 (3)	8782 (4)	40 (2)
C(36)	5450 (5)	6487 (4)	7956 (4)	49 (2)
C(37)	4803 (6)	5810 (4)	7824 (4)	70 (3)
C(38)	4755 (7)	7119 (4)	7651 (5)	77 (3)
C(39)	6425 (6)	6431 (5)	7473 (5)	85 (3)
C(40)	2483 (12)	1118 (8)	1599 (9)	112 (5)
C(41)	2408 (11)	735 (7)	2248 (8)	104 (5)
C(42)	1455 (14)	1522 (10)	1526 (9)	162 (7)
C(43)	3129 (14)	1140 (9)	967 (9)	161 (7)
C(44)	2968 (25)	1319 (16)	2131 (17)	67 (10)
C(45)	1978 (30)	374 (21)	1119 (22)	94 (13)
C(46)	1826 (31)	762 (20)	1599 (22)	93 (12)
C(47)	2771 (23)	918 (15)	2190 (16)	50 (8)

[a] Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

during full-matrix least-squares refinements was $\sum w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2(I)$. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 8. The positions of the hydrogen atoms of the methylene and phenyl groups were placed at calculated positions with d(C–H) = 0.96 Å and group isotropic thermal parameters, while the methyl groups were treated as rigid bodies, each with three rotational variables. The phenolic hydrogen atom in **1** was located in the final difference Fourier map and included in the refinement. For **1** all non-hydrogen atoms were refined with anisotropic thermal parameters whereas for **2** due to the relatively low number of unique reflections obtained only the non-hydrogen atoms forming the FeO_3N_3 octahedron and the methylene C atoms of the 1,4,7-triazacyclononane skeleton were refined with anisotropic thermal parameters; all other C atoms were refined isotropically. The acetylacetone molecule in **2** is disordered. It was not possible to completely resolve this disorder. Atom coordinates of **1** and **2** are given in Tables II and III, respectively.

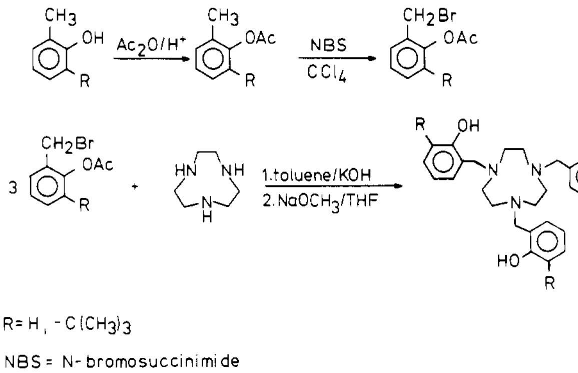
Results and Discussion

Syntheses. The ligands H_3L^1 and H_3L^2 are produced in good yields by the reaction of 1,4,7-triazacyclononane and the corresponding 2-(bromomethyl)phenyl acetate and KOH in toluene. 2-(Bromomethyl)phenyl acetate was prepared according to a published procedure,[6] and 2-(bromomethyl)-6-*tert*-butylphenyl acetate was prepared analogously from 6-*tert*-butyl-*o*-cresol, which was converted to the acetate in acetic anhydride and subsequently brominated at the methyl group. The general route is given in Scheme I. The crude products obtained from the reaction mixtures were found to be pure enough for the syntheses of transition-metal complexes.

---

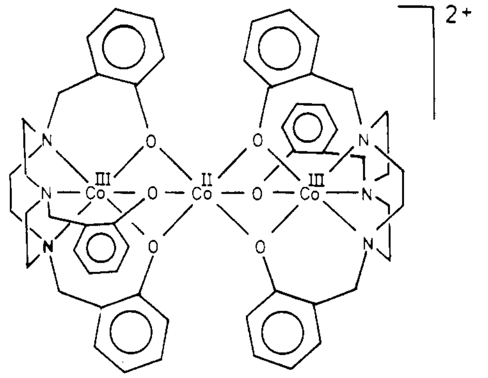
(8) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Scheme I



The ligands H_3L^1 and H_3L^2 form stable complexes L^1M^{III} and L^2M^{III} with trivalent metal complexes in a variety of polar solvents, e.g. $Fe(OH_2)_6^{3+}$ or $Fe(acac)_3$, or, alternatively, with divalent redox-active metal ions, e.g. Mn(II) or Co(II), in the presence of oxygen. Thus, complexes L^1Fe^{III} and L^1Mn^{III} were isolated as microcrystalline solids that are effectively insoluble in all common protic and aprotic solvents. In contrast, the neutral complexes L^2Mn^{III}, L^2Co^{III}, and L^2Fe^{III} are readily dissolved in organic solvents (acetone, alcohols, CH_3CN, CCl_4) but insoluble in water. The crystal structure determination of $[L^2Fe]$acacH shows that the ferric ion is coordinated to three tertiary amine nitrogen atoms and three phenolate oxygen atoms. The same structure is proposed for the corresponding manganese(III) and cobalt(III) species.

The reaction of $Co(BF_4)_2{\cdot}6H_2O$ with H_3L^1 in acetone in the presence of air affords within 12 h a pink precipitate that contains the coordinated trianion of the ligand, cobalt ions, and BF_4^- anions in the ratio 2:3:2. The salt is soluble in water; it may be recrystallized from hot methanol or acetone. From temperature-dependent magnetic susceptibility measurements in the temperature range 98–293 K, a temperature-independent magnetic moment of 5.35 μ_B/three cobalt ions has been deduced. This indicates the presence of one octahedral, high-spin cobalt(II). We propose the following trinuclear structure for $[L_2Co_3](BF_4)_2{\cdot}H_2O$. The trinuclear dication contains two diamagnetic Co(III) ions with a CoN_3O_3 donor set and one Co(II) center that is coordinated to six phenolate bridging oxygen atoms in an octahedral or trigonal-prismatic fashion.



This proposal is completely analogous to a similar complex with ethanolamine ligands, $[Co^{II}(Co^{III}(OCH_2CH_2NH_2)_3)_2]^{2+}$, the crystal structure of which has been determined.[9] The Co^{2+} ion is in a trigonal-prismatic environment of six μ-(alkoxo) bridging oxygen atoms.

The mononuclear diamagnetic green species L^2Co^{III} was prepared from the reaction between $Co(acac)_2$ and H_3L^2 in acetone in the presence of air.

Copper(II) forms the five-coordinate green species HL^1Cu^{II}, where one pendant phenolic arm is not bound to the metal center (see below). With H_3L^2 two different species were obtained when a mixture of $Cu(ClO_4)_2{\cdot}6H_2O$ and H_3L^2 in methanol was heated to reflux for 0.5 or 4 h. Upon addition of $NaClO_4$ green crystals of the composition $[H_2L^2Cu]ClO_4$ precipitated when the reaction mixture was heated to reflux for 30 min and a few drops of 1 M $HClO_4$ were added. Red crystals precipitated from the same reaction mixture when the solution was heated to reflux for 4 h but without addition of $HClO_4$. This material contains one sodium cation/copper ion as was established from elemental analysis. It is formulated as $[HL^2Cu]NaClO_4$. A preliminary structure determination of the green form $[H_2L^2Cu]ClO_4$ shows that the copper ion is in a distorted square-based-pyramidal environment comprised of three amine nitrogen atoms (two basal and one apical) and two oxygen atoms of a coordinated phenolate arm and a coordinated phenolic pendant arm. One phenolic pendant arm is not coordinated and bent away from the CuO_2N_3 entity. The red form $[HL^2Cu]NaClO_4$ is a mixed salt that contains the neutral molecule HL^2Cu^{II} and sodium perchlorate. We propose that the copper ions are also in a square-based-pyramidal or trigonal-bipyramidal environment of three amine nitrogen atoms and *two* phenolate anions (as in HL^1Cu^{II}). Figure 1 shows the structures for $[HL^1Cu^{II}]$ (green) and $[H_2L^2Cu^{II}](ClO_4)$ (green). From methanolic solutions of the red form green crystals of $[H_2L^2Cu](ClO_4)$ were obtained upon addition of a few drops of $HClO_4$, and the red form was regenerated by addition of base.

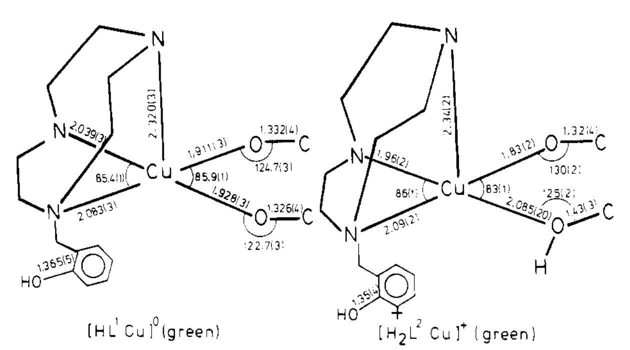


Figure 1. Schematic representation of the CuN_3O_2 cores in green crystals of HL^1Cu^{II} and $[H_2L^2Cu^{II}](ClO_4)$ as is established from X-ray structure determinations. The proton on the coordinated phenolic group in $[H_2L^2Cu^{II}](ClO_4)$ has not been located. Its presence is inferred from the subtle differences of bond lengths and angles compared to those of the coordinated phenolate groups.

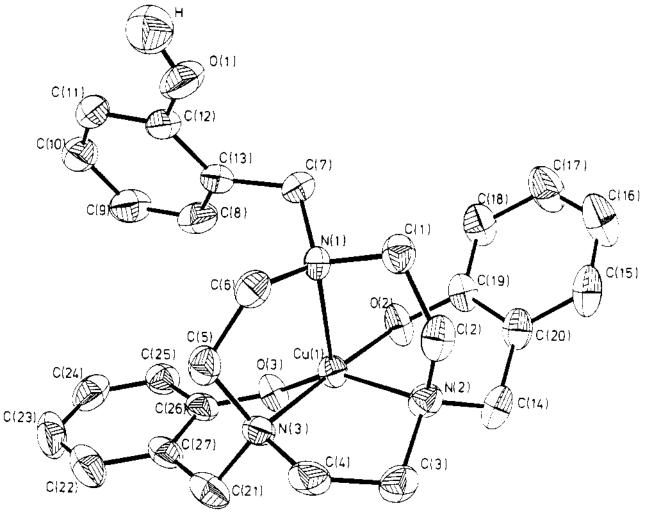


Figure 2. Structure of the neutral molecule in green crystals of **1**.

Crystal Structures of HL^1Cu^{II} (1) and $[L^2Fe^{III}]$acacH (2). Green crystals of **1** consist of neutral HL^1Cu^{II} molecules (Figure 2). Table IV summarizes selected bond distances and angles. The Cu^{2+} ions are in a distorted square-based-pyramidal environment of three amine nitrogen atoms and two phenolate oxygen atoms. As usual, the apical Cu–N bond distance is significantly longer than the corresponding two basal distances; the basal Cu–O

---

[9] Bertrand, J. A.; Kelley, J. A.; Vassian, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 2394.

Table IV. Selected Bond Distances (Å) and Angles (deg) in HL^1Cu^{II} (**1**)

Cu(1)–N(1)	2.320 (3)	Cu(1)–N(2)	2.083 (3)
Cu(1)–N(3)	2.039 (3)	Cu(1)–O(2)	1.928 (3)
Cu(1)–O(3)	1.911 (3)	O(1)–H	0.94 (4)
O(1)–C(12)	1.365 (5)	O(2)–C(19)	1.332 (4)
O(3)–C(26)	1.326 (4)	O(1)···O(2)′	2.623 (6)
O(2)···H	1.701 (50)		
N(1)–Cu(1)–N(2)	80.7 (1)	N(1)–Cu(1)–N(3)	82.3 (1)
N(2)–Cu(1)–N(3)	85.4 (1)	N(1)–Cu(1)–O(2)	99.3 (1)
N(2)–Cu(1)–O(2)	93.1 (1)	N(3)–Cu(1)–O(2)	177.6 (1)
N(1)–Cu(1)–O(3)	127.0 (1)	N(2)–Cu(1)–O(3)	152.1 (1)
N(3)–Cu(1)–O(3)	94.5 (1)	O(2)–Cu(1)–O(3)	85.9 (1)
C(12)–O(1)–H	103 (2)	Cu(1)–O(2)–C(19)	122.6 (3)
Cu(1)–O(3)–C(26)	124.7 (3)		

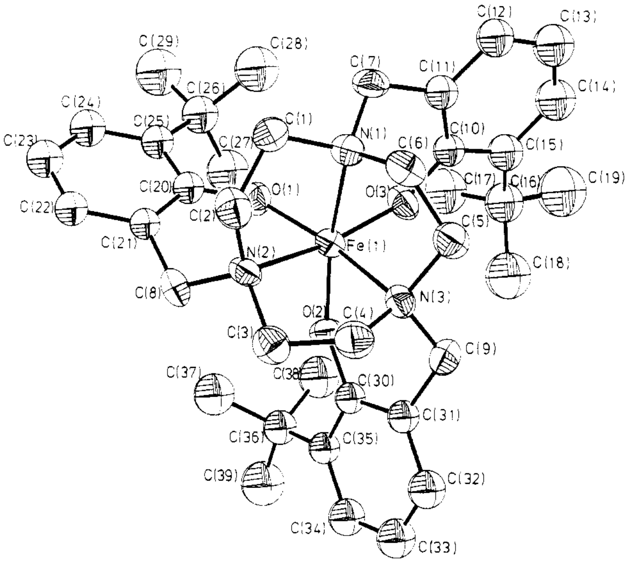


Figure 3. Structure of the neutral molecule in $[L^2Fe^{III}]$acacH.

distances are quite short and agree well with the phenolate–copper distances in $[Cu(EHPG)]^{2-}$, where EHPG represents ethylenebis[(*o*-hydroxyphenyl)glycine].[10] One phenolate pendant arm is not bound to the metal ion and is protonated. This phenolic group of one molecule forms a short hydrogen bond to a coordinated phenolate oxygen (O(2)) of a second molecule. Consequently, the Cu–O(2) distance is slightly longer than the Cu–O(1) bond length. The neutral molecules are thus linked to form a chain in crystals of **1**. It is noted that a preliminary investigation of the green form of $[H_2L^2Cu^{II}](ClO_4)$ by X-ray crystallography[11] has shown that the coordination geometry of the Cu^{2+} ion is also square-based pyramidal. The Cu^{2+} ion is coordinated to three amine nitrogen atoms, one phenolic oxygen, and one phenolate oxygen atom (the last two are in the basal plane); the third phenolic pendant arm is not bound to the Cu^{2+} center and is bent away as in **1**. Figure 1 emphasizes the small differences of Cu–N and Cu–O bond lengths in **1** and $[H_2L^2Cu](ClO_4)$.

Table V. Selected Bond Distances (Å) and Angles (deg) in $[L^2Fe^{III}]$acacH (**2**)

Fe(1)–O(1)	1.888 (4)	Fe(1)–O(2)	1.890 (4)
Fe(1)–O(3)	1.890 (4)	Fe(1)–N(1)	2.236 (5)
Fe(1)–N(2)	2.235 (5)	Fe(1)–N(3)	2.250 (5)
O(1)–C(10)	1.328 (8)	O(2)–C(20)	1.326 (8)
O(3)–C(30)	1.324 (7)		
O(1)–Fe(1)–O(2)	96.6 (2)	O(1)–Fe(1)–O(3)	98.0 (2)
O(2)–Fe(1)–O(3)	97.7 (2)	O(1)–Fe(1)–N(1)	87.3 (2)
O(2)–Fe(1)–N(1)	97.0 (2)	O(3)–Fe(1)–N(1)	163.7 (2)
O(1)–Fe(1)–N(2)	164.8 (2)	O(2)–Fe(1)–N(2)	87.3 (2)
O(3)–Fe(1)–N(2)	96.0 (2)	N(1)–Fe(1)–N(2)	77.7 (2)
O(1)–Fe(1)–N(3)	97.5 (2)	O(2)–Fe(1)–N(3)	164.5 (2)
O(3)–Fe(1)–N(3)	86.6 (2)	N(1)–Fe(1)–N(3)	77.4 (2)
N(2)–Fe(1)–N(3)	77.5 (2)	Fe(1)–O(1)–C(10)	137.5 (4)
Fe(1)–O(2)–C(20)	138.7 (4)	Fe(1)–O(3)–C(30)	139.1 (4)

Table VI. Electronic Spectral Data[a] and Magnetic Properties

compd	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	μ_{eff}, μ_B
H_3L^1	275 (2400), 280 (sh)	
$Na_3[L^1]$	293 (3400)	
H_3L^2	280 (6400), 276 (sh)[b]	
$K_3[L^2]$	312 (12 500)	
L^1Mn^{III}	620 (540), 367 (1800), 283 (10 200)	4.8
L^1Fe^{III}	459 (3800), 315 (sh), 281 (7500)	not measd
$[(L^1Co)_2Co](BF_4)_2 \cdot H_2O$	546 (980), 362 (2600)	5.35[c]
HL^1Cu^{II}	644 (210), 401 (800), 286 (8100)	not measd
L^2Fe^{III}	479 (5600), 324 (6300), 282 (12 400), 243 (12 500)	5.8
L^2Mn^{III}	658 (650), 379 (3250), 282 (13 200)	4.8
L^2Co^{III}	581 (490), 398 (sh), 363 (2590)	diamagnetic
$[H_2L^2Cu^{II}]ClO_4$ (green)	670 (390), 581 (1040), 450 (1050), 320 (5420), 293 (12 000), 279 (15 000)	1.7
$[HL^2Cu^{II}]NaClO_4$ (red)	850 (120), 670 (390), 495 (1400), 315 (6700), 292 (11 000), 279 (14 000)	1.7

[a] Measured in CH_3CN except as indicated otherwise. [b] Measured in CH_2Cl_2. [c] μ_{eff} per trinuclear complex.

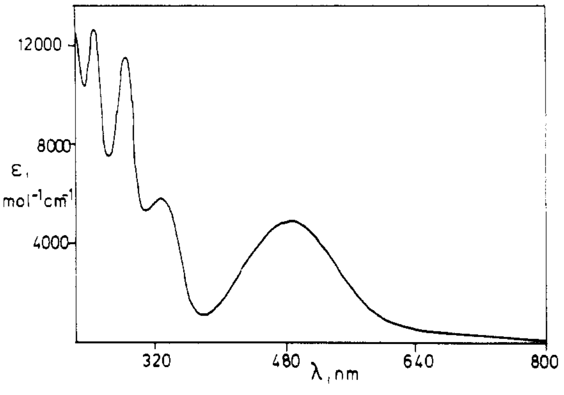


Figure 4. Electronic spectrum of L^2Fe^{III} in CH_3CN.

Red-brown crystals of **2** consist of L^2Fe^{III} molecules (Figure 3) and uncoordinated 2,4-pentanedione (acacH) molecules that are disordered. The ferric ion is in a pseudooctahedral environment comprised of three tertiary amine nitrogen atoms and three phenolate oxygen atoms (FeN_3O_3). The pendant arms form three six-membered chelate rings. The Fe–N bond lengths are equivalent within experimental uncertainty and rather long (average 2.240 Å) (Table V). This is typical for octahedral high-spin ferric ions. The average Fe–O distance of 1.889 Å is quite short and compares well with other ferric phenolate complexes.[12,13] The N–Fe–N bond angles are compressed (average 77.6°) due to steric constraints of the 1,4,7-triazacyclononane backbone of the ligand L^2, whereas the O–Fe–O angles are expanded (average 97.4°).

Electronic Spectra and Magnetic Properties. Electronic spectral data and magnetic properties of new compounds are summarized

---

[10] Riley, P. E.; Pecoraro, V. L.; Carrano, C. J.; Raymond, K. N. *Inorg. Chem.* **1983**, *22*, 3096.

[11] Crystal data for green $[H_2L^2Cu](ClO_4)$: orthorhombic space group $P2_12_12_1$, with a = 10.957 (7) Å, b = 14.330 (6) Å, c = 27.450 (10) Å, Z = 4. A total 1022 unique reflections ($I > 2.5\sigma(I)$) and 242 refined parameters yielded a preliminary structure. The CuN_3O_2 core is shown in Figure 1. The present agreement factor is 0.086. The crystal chosen is not ideally suited for X-ray crystallography, and attempts to grow better single crystals with a different anion are underway.

[12] (a) Bailey, N. A.; Cummins, D.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1976**, *18*, L13. (b) Bailey, N. A.; Cummins, D.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1981**, *50*, 111.

[13] Ainscough, E. W.; Brodie, A. M.; Plowman, J. E.; Brown, K. L.; Addison, A. E.; Gainsford, A. R. *Inorg. Chem.* **1980**, *19*, 3655.

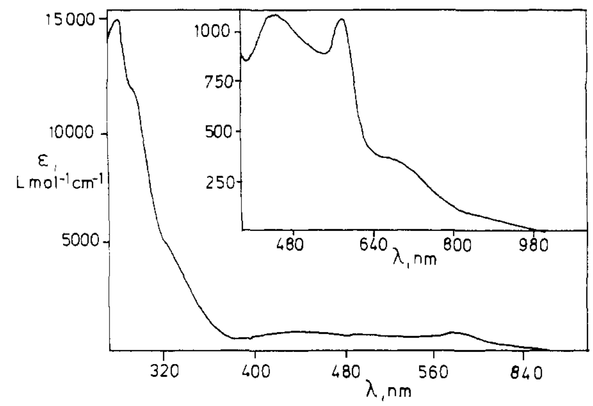


Figure 5. Electronic spectrum of $[H_2L^2Cu](ClO_4)$ (green) in CH_3CN.

in Table VI. The electronic spectra of the uncoordinated ligands H_3L^1 and H_3L^2 exhibit two intense absorption maxima in the 200–300-nm region, whereas the corresponding deprotonated phenolate forms show only one intense absorption maximum, which is shifted to higher wavelengths in comparison with the protonated forms. These data are in agreement with the UV-spectra of phenol (λ_{max} = 270 nm; $\epsilon = 1.45 \times 10^3$ L mol^{-1} cm^{-1}) and the phenolate anion (λ_{max} = 287 nm (2600)). These bands are assigned to $\pi \rightarrow \pi^*$ transitions. Inter- and intramolecular hydrogen bonding between the phenolic groups and the amine nitrogen atoms of the 1,4,7-triazacyclononane backbone of H_3L^1 and H_3L^2 in solution may cause the observed splitting of the $\pi \rightarrow \pi^*$ transition. Intramolecular N···H–O hydrogen bonding has been detected in the solid-state structure of 1,4,7-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane.[4]

Figure 4 shows the electronic spectrum of L^2Fe^{III} in acetonitrile. The band at 478 nm is assigned to a phenolate-to-iron(III) transition; upon removal of the *tert*-butyl groups this band is shifted to 459 nm in L^1Fe^{III} because the $-C(CH_3)_3$ groups have more electron-donating capacity than the phenyl ring protons in L^1Fe^{III}.[14] Gaber and co-workers[15] have assigned this band to a transition from pπ orbitals on the phenolate oxygen atoms to the half-filled dπ^* orbitals on Fe(III). It has also been proposed that the absorptivity of the visible band is roughly additive for successive phenolate binding ((1–2) $\times 10^3$ L mol^{-1} cm^{-1}/ligand).[16] This appears to hold for L^1Fe^{III} and L^2Fe^{III}, both of which contain three phenolate ligands. For the latter the 479-nm band has a molar extinction coefficient of 5.6×10^3 L mol^{-1} cm^{-1} whereas for the former a somewhat lower intensity of 3.8×10^3 L mol^{-1} cm^{-1} has been observed. The absorption maximum at ≈320 nm in both compounds may be assigned to an amine-to-iron(III) charge transfer that is practically not affected by the nature of the substituted phenolate rings. This absorption maximum has been observed in a number of (1,4,7-triazacyclononane)iron(III) complexes.[17] The intense absorption at 282 nm corresponds to the $\pi \rightarrow \pi^*$ transition. On the other hand, Gaber et al. suggested that the band at ≈320 nm may be assigned to p$\pi \rightarrow$ dσ^* charge transfer of the phenolate oxygen atoms.[15]

L^1Fe^{III} and L^2Fe^{III} are both high-spin ferric complexes, as is judged from their temperature-independent magnetic moments (98–298 K) (Table VI).

The electronic spectra of L^1Mn^{III} and L^2Mn^{III} are also quite similar; a fairly intense absorption maximum in the visible region and one band in the near-UV region and the π–π^* transition in the UV region of the coordinated phenolates are observed, respectively. The absorption in the visible is shifted to the red region in L^2Mn^{III} as compared to L^1Mn^{III}. The comparatively low intensity of this band may be indicative of a d–d transition of the

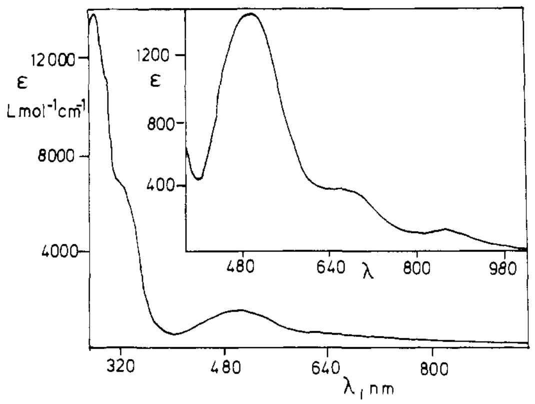


Figure 6. Electronic spectrum of $[HL^2Cu]NaClO_4$ (red) in CH_3CN.

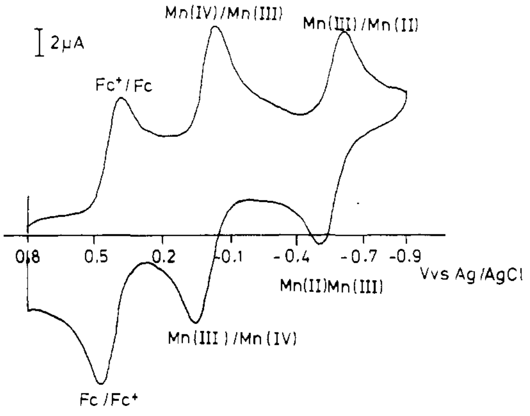


Figure 7. Cyclic voltammograms of L^2Mn^{III} in CH_2Cl_2 at a glassy-carbon working electrode (0.1 M $[(n\text{-butyl})_4N]PF_6$ supporting electrolyte; 22 °C) at scan rate 200 mV s^{-1} with the internal standard ferrocene.

high-spin manganese(III) ions ($^5E_g \rightarrow {}^5T_{2g}$ in O_h symmetry). The magnetic moment of 4.8 μ_B (98–298 K) is in excellent agreement with the spin-only value for a high-spin manganese(III) ion.

L^2Co^{III} is diamagnetic whereas the trinuclear complex $[(L^1Co)_2Co](BF_4)_2 \cdot H_2O$ has a temperature-independent magnetic moment of 5.35 μ_B, which is typical for a high-spin cobalt(II) ion in an octahedral ligand environment.

Figure 5 shows the electronic spectrum of green $[H_2L^2Cu^{II}](ClO_4)$ in CH_3CN and Figure 6, that of red $[HL^2Cu^{II}]NaClO_4$ in CH_3CN. For $[HL^2Cu]NaClO_4$ (red) two d–d transitions of relative low intensity in the visible region are characteristic for Cu^{2+} ions in a square-based-pyramidal or trigonal-bipyramidal ligand environment. The intense absorption at 495 nm is assigned to a phenolate-to-copper(II) transition whereas three very intense bands at 315, 292, and 279 nm are due to $\pi \rightarrow \pi^*$ transitions of two coordinated phenolates and one uncoordinated phenolic pendant arm. Interestingly, in the spectrum of $[H_2L^2Cu]ClO_4$ only one weak d–d transition and *two* moderately intense phenolate-to-copper charge-transfer bands at 581 and 450 nm are observed. This splitting of the latter band may reflect the fact that this compound contains a coordinated phenolate *and* a phenolic group. The spectrum of HL^1Cu^{II} is very similar to that of $CuEHPG^{2-}$ (EHPG = ethylenebis[(*o*-hydroxyphenyl)glycine]).[18]

The electronic spectra of the new Fe(III), Mn(III), Co(III), and Cu(II) complexes resemble those of the correspondingly metalated biomolecules of transferrin and lactoferrin.[19,20]

Electrochemistry. Due to their very low solubility in all common solvents we have not been able to record cyclic voltammograms of L^1M^{III} (M = Fe, Mn) complexes. In contrast, their L^2M^{III} counterparts are soluble in acetonitrile or CH_2Cl_2. The cyclic

---

(14) Pyrz, J. W.; Roe, A. L.; Stern, J.; Que, L., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 614.

(15) Gaber, B. P.; Miskowski, V.; Spiro, T. G. *J. Am. Chem. Soc.* **1974**, *96*, 6868.

(16) Ackermann, G. A.; Hesse, D. *Z. Anorg. Allg. Chem.* **1970**, *375*, 77.

(17) Drueke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Fleischhauer, H.-P.; Gehring, S.; Haase, W. *J. Am. Chem. Soc.* **1989**, *111*, 8622.

(18) Patch, M. G.; Simolo, K. P.; Carrano, C. J. *Inorg. Chem.* **1982**, *21*, 2972.

(19) Aisen, P.; Aasa, R.; Redfield, A. G. *J. Biol. Chem.* **1969**, *244*, 4628.

(20) Ainscough, E. W.; Brodie, A. M.; Plowman, J. E. *Inorg. Chim. Acta* **1979**, *33*, 149.

voltammogram of L_2Fe^{III} in CH_2Cl_2 (0.1 M [(*n*-butyl)$_4$N]PF_6) at a glassy-carbon working electrode shows one quasi-reversible one-electron-transfer wave ($E_{1/2}$ = −1.86 V vs Fc^+/Fc) in the potential range +0.3 to −1.8 V vs Ag/AgCl, which is assigned to the couple $L^2Fe^{III}/[L^2Fe^{II}]^-$. This negative redox potential is in good agreement with other (phenolate)- or (catecholate)iron(III) complexes, e.g. $[Fe(salen)PD]^{-/2-}$ (−1.87 V vs Fc^+/Fc) and $[Fe(salen)DBcat]^{-/2-}$ (−2.0 V vs Fc^+/Fc).[21] It indicates the enormous stabilization of the ferric phenolate over the ferrous phenolate species.

The cyclic voltammogram of L^2Mn^{III} in CH_2Cl_2 (0.1 M [(*n*-butyl)$_4$N]PF_6) is shown in Figure 7. Two reversible one-electron-transfer waves are detected in the potential range 0.8 V to −0.9 V vs Ag/AgCl at $E^1_{1/2}$ = −0.45 V and $E^2_{1/2}$ = −0.982 V vs Fc^+/Fc. The first process corresponds to the Mn(IV)/Mn(III) couple, and the second, to the Mn(III)/Mn(II) couple. The reversibility of the latter process is impaired at slower scan rates (<200 mV s^{-1}) due to the lability of the reduced Mn(II) form. Similar redox chemistry has been reported for a series of manganese complexes containing a Schiff base ligand derived from substituted salicylaldehydes.[22]

Due to severe absorption effects of L^2Co^{III} in CH_3CN or CH_2Cl_2 at the surface of the working electrode (glassy-carbon or Pt-button), it has not been possible to obtain a reproducible cyclic voltammogram of this species.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: For complexes **1** and **2**, listings of positional parameters, thermal parameters, crystallographic data (Table S1), calculated positions of hydrogen atoms, and bond lengths and bond angles (11 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

---

(21) Heistand, R. H., II; Lauffer, R. B.; Fikrig, E.; Que, L., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2789.

(22) Coleman, W. M.; Bogges, R. K.; Hughes, J. W.; Taylor, L. T. *Inorg. Chem.* **1981**, *20*, 1253.

Contribution from the Departments of Chemistry, Southwest Texas State University, San Marcos, Texas 78666, University of Texas at Austin, Austin, Texas 78712, and University of Michigan, Ann Arbor, Michigan 48109-1055

Monomeric and Dimeric Vanadium(IV) and -(V) Complexes of *N*-(Hydroxyalkyl)salicylideneamines: Structures, Magnetochemistry, and Reactivity

Carl J. Carrano,[*,†] Christine M. Nunn,[‡] Roger Quan,[§] Joseph A. Bonadies,[§,‖] and Vincent L. Pecoraro[*,§]

Received June 28, 1989

The *N*-(hydroxyalkyl)salicylideneamine ligands ($H_2SALAHE$ = 2-(salicylideneamino)-1-hydroxyethane; $H_2SALAHP$ = 3-(salicylideneamino)-1-hydroxypropane; $H_2SALAMHP$ = 2-(salicylideneamino)-2-methyl-1-hydroxypropane; $H_2SALAMHE$ = 2-(salicylideneamino)-2-methyl-1-hydroxyethane [or 2-(salicylideneamino)-1-hydroxypropane]; $H_2SALATHM$ = tris(hydroxymethyl)(salicylideneamino)methane) form monomeric and dimeric complexes when reacted with VO^{2+} salts in organic solvents. When a 2:1 ligand to metal ratio is used in the synthesis, the mononuclear $VO(HSALAHE)_2$ (**1**) crystallizes as a dark green solid with X-ray diffraction analysis demonstrating it to be a five-coordinate species with the ligands bound in a bidentate fashion by using the phenolate and imine nitrogen atoms. When a 1:1 ligand to metal ratio is used and the reaction maintained strictly anaerobic, a dimer of composition $[VO(SALAHE)]_2$ (**3**) is recovered. X-ray crystallography demonstrates that the ligand is a tridentate dianion in this complex, which is a dialkoxy-bridged dimer with a syn orientation of vanadyl oxygen atoms. This structure is in contrast to a polymeric material of the same composition $[VO(SALAHE)]_n$ (**2**), which is thought to be an infinite spin ladder. Magnetic exchange in **2** (1.01 μ_B/V) is slightly greater than in **3** (1.52 μ_B/V), which probably reflects the larger extent of σ overlap between d_{xy} orbitals of the two vanadium atoms in the planar **2** as opposed to the bent **3**. These vanadium(IV) dimers can be converted to an unusual V(V) dimer of composition $[V^VOL]_2O$. An X-ray diffraction analysis of the SALAMHP derivative **4c** shows that the ligands are again tridentate; however, one alkoxide acts as a weak bridge while the other is nonbridging. The strongest link between the vanadium atoms is a nonlinear oxo group that is part of the $V_2O_3^{4+}$ core. Crystallographic parameters for **1**, **3**, and **4c** are as follows. $VO(SALAHE)_2$ (**1**) ($C_{18}H_{20}N_2O_5V$): MW, 395.31; *a*, 10.301 (2) Å; *b*, 8.733 (3) Å; *c*, 20.575 (5) Å; β, 104.19 (2)°; *V*, 1794.4 (6) Å^3; monoclinic ($P2_1/c$); Z = 4; for 2953 unique data ($3 < 2\theta < 48°$) and 2010 data with $I > 2\sigma(I)$, the structure refined to $R(F_o)$ = 0.062. $[VO(SALAHE)]_2$ (**3**) ($C_{18}H_{18}N_2O_6V_2$): MW, 460; *a*, 22.530 (3) Å; 6.530 (6) Å; *c*, 13.115 (15) Å; β, 93.04 (10)°; *V*, 1927 (4) Å^3; monoclinic ($P2_1/c$); Z = 4; for 2510 unique data ($0 < 2\theta < 45°$) and 1387 data with $I > 2\sigma(I)$, the structure refined to $R(F_o)$ = 0.077. $[VO(SALAMHP)]_2O$ (**4c**) ($C_{22}H_{26}N_2O_7V_2$): MW, 532.4; *a*, 33.929 (6) Å; *b*, 7.203 (2) Å; *c*, 19.618 (5) Å; β, 98.97 (2)°; *V*, 4736.1 (8) Å^3; monoclinic ($C2/c$); Z = 8; for 4248 unique data ($3 < 2\theta < 50°$) and 2662 data with $I > 3\sigma(I)$, the structure refined to $R(F_o)$ = 0.052.

Introduction

Vanadium is receiving considerable attention as a biologically important metal due to the recent discovery of the first two vanadoenzymes (bromoperoxidase from marine algae[1,2] and nitrogenase from *Azotobacter vinelandii*[3]). The nitrogenase most likely contains a modified form of the FeMo cofactor in which vanadium replaces molybdenum.[4-6] Much less is known about metal ligation in the bromoperoxidase.[7-12] It has been established that the catalytically active form of the enzyme contains a mononuclear V(V) center and that neither a metal sulfide cluster nor a vanadoporphyrin is an appropriate description of the active site. Presumably amino acid residues such as aspartate, glutamate, serine, threonine, tyrosine, and histidine supply the majority of heteroatom donors, although one or two terminal oxo groups are probably present.

[†] Southwest Texas State University.

[‡] University of Texas at Austin.

[§] University of Michigan.

[‖] Present address: Dow Chemical, USA, Midland, MI.

(1) Vilter, H. *Phytochemistry* **1984**, *23*, 1387.

(2) de Boer, E.; van Kooyk, Y.; Tromp, M. G. M.; Plat, H.; Wever, R. *Biochim. Biophys. Acta* **1986**, *869*, 48.

(3) Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature (London)* **1986**, *322*, 388.

(4) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 702.

(5) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 711.

(6) Morningstar, J. E.; Johnson, M. K.; Case, E. E.; Hales, B. J. *Biochemistry* **1987**, *26*, 1795.

(7) de Boer, E.; Tromp, M. G. M.; Plat, H.; Krenn, B. E.; Wever, R. *Biochim. Biophys. Acta* **1986**, *872*, 104.

(8) de Boer, E.; Wever, R. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 409.

(9) de Boer, E.; Boon, K.; Wever, R. *Biochemistry* **1988**, *27*, 1629.

(10) de Boer, E.; Wever, R. *J. Biol. Chem.* **1988**, *263*, 12326.

(11) Wever, R.; Krenn, B. E.; de Boer, E.; Offenberg, H.; Plat, H. In *Oxidases and Related Redox Systems*; King, T. E., Mason, H. S., Morrison, M., Eds.; Alan R. Liss Publishers: New York, 1988; p 477.

(12) Everett, R. R.; Butler, A. *Inorg. Chem.* **1989**, *28*, 393.