6080 *Inorg. Chem.* **1997,** *36,* 6080−6085

Tsalen- and Tsalpn-Based Nickel Complexes with Two Aldehyde Functionalities as Potential Synthons for Thiophenolate-Containing Di- and Polynucleating Acyclic and Macrocyclic Ligands

Aase Christensen,[†] Holger S. Jensen,[†] Vickie McKee,*[‡] Christine J. McKenzie,*[†] and Maria Munch[†]

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark, and
School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

Received June 10, 1997[⊗]

Tsalen- and tsalpn-based nickel complexes with aldehyde functionalities have been prepared (tsalen = *N*,*N*′-ethylenebis(thiosalicylideneaminato)$^{2-}$ and tsalpn = *N*,*N*′-propane-1,3-diyl(thiosalicylideneaminato)$^{2-}$). One of the complexes has been structurally characterized: Ni(pftp) (pftp = *N*,*N*-ethylene(6-formyl-4-methyl-2-methyliminatothiophenolato)$^{2-}$) crystallizes in the monoclinic space group $C2/c$ with $a = 28.761(7)$, $b = 8.582(2)$, $c = 7.841(4)$ Å; $\beta = 98.92(3)°$, and $Z = 4$. Ni(pftp) and Ni(eftp) (efpt = *N*,*N*-ethylene(6-formyl-4-methyl-2-methyliminatothiophenolato)$^{2-}$) were used as synthons for acyclic and macrocyclic complexes and a prototype of each has been structurally characterized. The Schiff base derivative of Ni(pftp) and 2-(2-aminoethyl)pyridine gives the acyclic complex, Ni(peptp) (peptp =*N*,*N*-propane-1,3-diyl(6-(*N*-(2-ethylpyridyl)iminomethyl)-4-methyl-2-methyliminatothiophenolato)$^{-}$) with the two ethylpyridyl arms furnishing an "open site", which in this complex is vacant, and a "closed site", in which the Ni^{2+} is located. Ni(peptp) crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.247(7)$, $b = 21.886(8)$, $c = 15.662(9)$ Å; $\beta = 92.58(6)°$, and $Z = 4$. Schiff base condensation of Ni(pftp) with diaminopropane gave two different macrocyclic dinickel complexes $[L^1Ni_2](ClO_4)_2$ and L^2Ni_2. L^1 and L^2 are the 2 + 2 and 4 + 4 macrocycles, respectively, comprising two propylenediamine and two thiocresol units and four propylenediamine and four thiocresol units, respectively. Crystals of L^2Ni_2 (L^2 = (10,23,36,49-tetramethyl-13,26,39,52-tetramercapto-2,6,15,19,28,32,41,45-octaaza-1,7,14,20,27,33,40,46-octaene[7.7.7.7]-metacyclophane) are of poor quality and crystallize in the $C2/c$ space group with $a = 31.517(14)$, b =8.980(2), $c = 26.822(12)$ Å; $\beta = 117.17(2)°$, and $Z = 4$.

Introduction

Complexes of thiolate ligands have attracted increased attention in recent years because of the recognition of the biological significance of metal−cysteine sulfur interactions. Monodentate and bridging cysteine sulfur atoms have been found coordinated to Fe, Ni, Zn, Mo, and Cu in metalloenzymes. In the case of cysteine-bridged systems, both homodinuclear and heterodinuclear centers are known. The recent structural elucidation of cytochrome *c* oxidase from bovine heart[1a] and *Paracoccus denitrificans*[1b] shows that the Cu_A site involved in electron transport is a μ_2-dithiolate-bridged dicopper center. This dinuclear center had been difficult to assign spectroscopically, not only because of the presence of several other metal ions, including a copper ion, but also because of the paucity of complexes with two thiolate sulfur atoms bridging between two copper atoms in Cu^{II}/Cu^{II} or Cu^{I}/Cu^{II} oxidation states as spectroscopic models.[2] The X-ray structural solution of hydrogenase from *Desulfovibrio gigas*[3] shows that the nickel atom at the active site is bound by four cysteine residues, two of which bridge to a second metal ion which is most likely iron. Early attempts to model the active site of hydrogenase have been largely directed toward the synthesis of mononuclear nickel thiolate complexes.[4] In light of the recent crystal structure of hydrogenase, it is now recognized that complexes containing nickel and a second metal ion in which the metal atoms are bridged by thiolate sulfur atoms are pertinent. This result has already spurred synthetic chemists on with the goal of preparing thiolate-bridged Ni−Fe complexes as models for the active site.[5]

We have been working on the preparation of thiolate complexes of the biologically relevant transition metals in the hope that these complexes will be useful as spectroscopic and perhaps even functional model complexes for the thiolate−metal systems found in Nature. In particular, we are interested in discovering stepwise syntheses by which heteronuclear and mixed-valent complexes might be prepared. There are two main problems to overcome in the preparation of complexes of thiolate ligands: oxidation of the ligands to disulfides with concomitant metal reduction and the uncontrolled formation of multinuclear complexes due to the propensity of thiolate sulfur atoms to bridge between metal atoms.[6]

In this article, we present a new strategy for the preparation of dithiophenolate-containing ligands and their complexes based on tsalen and tsalpn backbones (tsalen = *N*,*N*′-ethylenebis(thiosalicylideneaminato)$^{2-}$ and tsalpn = *N*,*N*′-propane-1,3-diyl(thiosalicylideneaminato)$^{2-}$). Two of the complexes described

---

[†] Odense University.

[‡] Queen's University.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) (a) Tsukihara, T.; Aoyama, H.; Yamashita, E.; Tomizaki, T.; Yamaguchi, H.; Shinzawa-Ito, K.; Nakashima, R.; Yaono, R.; Yoshikawa, S. *Science* **1995**, *269*, 1069−1074. (b) Iwata, S.; Ostermeier, C.; Ludwig, B.; Michel, H. *Nature* **1995**, *376*, 660−669.

(2) Houser, R. P.; Young, V. G.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 2101−2102.

(3) Volbeda, A.; Charon, M.-H.; Piras, C.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *Nature* **1995**, *373*, 580−587.

(4) Krüger, H. J.; Peng, G.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 734−742.

(5) (a) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421−1423. (b) Colpas, G. J.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1992**, *31*, 5053−5055. (c) Osterloh, F.; Saak, W.; Haase, D.; Pohl, S. *J. Chem. Soc., Chem. Commun.* **1996**, 777−778.

S0020-1669(97)00713-1 CCC: $14.00

below contain two aldehyde functionalities as handles for further reaction and are thus potentially useful building blocks for asymmetric homo- and heteronuclear dithiophenolate-bridged complexes of compartmental ligands. Noteworthy is the fact that complexes of the parent ligand tsalen^{2-} itself are rare,[7] and to our knowledge complexes of the parent molecule tsalpn^{2-} have not been reported. Thus, by marked contrast to their phenolate counterparts, salen^{2-}, *N,N*-ethylenebis(salicylideneaminato)$^{2-}$ and salpn^{2-} (*N,N′*-propane-1,3-diyl(salicylideneaminato)$^{2-}$), the coordination chemistry of these thiophenolate-containing ligands has been little exploited.

Experimental Section

Physical Measurements. NMR spectra were recorded at 250 MHz for ^{1}H NMR and 63 MHz for ^{13}C NMR on a Bruker AC 250 spectrometer. IR spectra were measured as KBr disks using a Hitachi 270-30 IR spectrometer. UV−visible absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Mass spectra were recorded with either a Varian MAT311A spectrometer (EI) or a Kratos MS-50 (FAB) instrument. Elemental analyses were carried out at the microanalytical laboratory of the H. C. Ørsted Institute, Copenhagen, Denmark.

Syntheses. [*N,N*-Ethylene(6-formyl-4-methyl-2-methyliminatothiophenolato)]nickel(II) (Ni(eftp)). 1,2-Ethanediamine (0.1490 g, 2.48 mmol) and $Ni(ClO_4)_2\cdot 6H_2O$ (0.3937g, 1.07 mmol) were dissolved in 10 mL of DMF. 2-(*N,N*-Dimethylcarbamoylthio)-5-methylisophthaldehyde[8] (0.3641 g, 1.45 mmol) in 5 mL of DMF was added and the mixture was heated to ca. 100 °C for 10 min. The yellow-brown Ni(eftp) crystallized on standing at room temperature. Yield 0.2746 g, 85%. Anal. Calcd for Ni(eftp)·dmf·0.5H$_2$O, $C_{23}H_{16}N_3O_{3.5}S_2Ni$: C, 52.79; H, 5.01; N, 8.03. Found: C, 52.24; H, 5.13; N, 8.46. FABMS: *m/z* 441 ([Ni(eftp)H]$^+$, 20%). UV−vis (CH_2Cl_2, λ, nm; ϵ, M^{-1} cm^{-1}): 310, 7261; 385, 4681; 460, 1804; 492, sh, 1224; 600, 274.

[*N,N*-Propane-1,3-diyl(6-formyl-4-methyl-2 methyliminatothiophenolato)]nickel(II) (Ni(pftp)). 1,3-Diaminopropane (0.1612 g, 2.17 mmol) and $Ni(ClO_4)_2\cdot 6H_2O$ (0.3807g, 1.04 mmol) were mixed in 10 mL of DMF. 2-(*N,N*-Dimethylcarbamoylthio)-5-methylisophthaldehyde (0.3781 g, 1.50 mmol) in 5 mL of DMF was added, and the mixture was warmed at ca. 100 °C for 10 min. Yellow-brown needles of the product were deposited at room temperature over a day. Yield 0.1953 g, 57%. Anal. Calcd for Ni(pftp)·H$_2$O, $C_{21}H_{22}N_2O_3S_2Ni$: C, 53.30; H, 4.69; N, 5.92. Found: C, 53.00; H, 4.23; N, 6.27. ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 25°, TMS): δ 10.85, s, 2H, CHO; 7.77, s, 2H, ArH; 7.61, s, 2H, ArH; 7.25, s, 2H, NCH; 3.9, t, $J = 0.01$, 4H, CH_2; 2.27, s, 3H, CH_3; 2.04, m, 2H, CH_2. ^{13}C NMR (125 MHz, $CDCl_2CDCl_2$, 25 °C, TMS): δ 193.66 CHO; 166.23, C=N; 147.34, 141,27, 134.94, 134.63, 133.34, ArC; 58.26, CH_2; 28.11, CH_2, 28.88, CH_3. EIMS: *m/z* 455 ([Ni(pftp)]$^+$, 20%). UV−vis (λ, nm; ϵ, M^{-1} cm^{-1}): 321, 19190; 399, 11759; 458, 4379; 605, 305.

[*N,N*-Propane-1,3-diyl(6-(*N*-(2-ethylpyridyl)iminomethyl)-4-methyl-2-methyliminatothiophenolato)]nickel(II) (Ni(peptp)). Ni(pftp) (54 mg, 0.12 mmol) and 2-(2-aminoethyl)pyridine (57 mg, 0.463 mmol) were mixed in 25 mL of acetonitrile. The suspension was heated under reflux for ca. 30 min during which time Ni(pftp) dissolved and the product precipitated as brown needles. Yield 58 mg, 74%. Anal. Calcd for Ni(peptp)·H$_2$O, $C_{35}H_{38}N_6OS_2Ni$: C, 61.68; H, 5.62; N, 12.33. Found C, 61.39; H, 5.30; N, 11.62. EIMS: *m/z* 663 ([peptpNi]$^+$, 100%). UV−vis (λ, nm; ϵ, M^{-1} cm^{-1}): 366, 6047; 454, 1775; 629, 166.

[(10,23-Dimethyl-13,26-dimercapto-2,6,15,19-tetraaza-1,7,14,20-tetraene[7.7.7.7]metacyclophane)dinickel]diperchlorate (L^1Ni_2]($ClO_4)_2$]. Ni(pftp), 1,3-diaminopropane, and $Ni(ClO_4)_2\cdot 6H_2O$ were combined in 1:1.5:1 proportions in a methanol/DMF mixture. The product crystallized as red crystalline blocks. Anal. Calcd for $[L^2Ni_2](ClO_4)_2\cdot$DMF, $C_{27}H_{26}N_4S_2Ni_2Cl_2O_9$: C, 39.65; H, 4.04; N, 8.90. Found: C, 40.12; H, 4.32; N, 9.32. FABMS: *m/z* 651, 90% $[L^1Ni_2](ClO_4)^+$; 550, 100%, $[L^1Ni_2]^+$.

(10,23,36,49-Tetramethyl-13,26,39,52-tetramercapto-2,6,15,19,-28,32,41,45-octaaza-1,7,14,20,27,33,40,46-octaene[7.7.7.7]-metacyclophane)dinickel (L^2Ni_2). This preparation is not optimized. Crystals of this complex for the crystallographic study were obtained from the reaction of Ni(pftp), $PdCl_2$, and 1,3-diaminopropane in 1:1: 1.5 proportions in acetonitrile. The brown powder that precipitated was collected and redissolved in warm DMF. The brown crystals used for the crystallography study were deposited over a period of several days at room temperature; FABMS, *m/z* 985 $[L^2Ni_2H]^+$. Sufficient quantities of L^2Ni_2 have not been obtained; hence, bulk elemental and spectroscopic analysis of this compound has not been possible.

X-ray Crystallography. Crystal data and details of structure determinations are listed in Table 1. Table 2 contains a list of selected bond distances and angles for Ni(pftp), Ni(peptp)·CH_3CN, and L^2Ni_2. Data for all three crystals were collected at 153 K on a Siemens P4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation. The data were corrected for Lorentz and polarization effects, and absorption corrections were applied to Ni(pftp) and Ni(peptp)·CH_3CN. The structures were solved by direct methods,[9] and all the data were used for refinement on F^2. Ni(pftp) and Ni(peptp)·CH_3CN were refined with all the non-hydrogen atoms assigned anisotropic atomic displacement parameters; hydrogen atoms were inserted at calculated positions with isotropic temperature factors riding on those of their carrier atoms.

Crystals of L^2Ni_2 were very small and gave a very weak data set; only 35% of reflections in the range $4 < 2\theta < 40°$ had $I > 2\sigma I$. This structure has not been fully refined, and although the main features of the complex are clear, the identity of the solvate molecules has not been unambiguously determined. A higher quality structure awaits the growth of better crystals.

All programs used in the structure refinements are contained in the SHELXL-93 package.[10]

Results and Discussion

The nickel complexes [*N,N′*-ethylene(6-formyl-4-methyl-2-methyliminatothiophenolato)]nickel(II), Ni(eftp), and [*N,N′*-propane-1,3-diyl(6-formyl-4-methyl-2-methyliminatothiophenolato)]nickel(II), Ni(pftp), were prepared by the route depicted in Figure 1. Under the conditions described in the Experimental Section, an aldehyde group on each of the thiocresol units derived from the carbamoyl sulfur-protected precursor has remained intact. The reason for this surprising result may not be electronic, i.e., a difference in reactivity of the second aldehyde group of each thiocresol unit, but rather thermodynamic: Ni(eftp) and Ni(pftp) are relatively insoluble and therefore precipitate readily from reaction mixtures. Despite

---

(6) (a) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem.* **1992**, *31*, 161−163. (b) Capdevila, M.; Gonzáles-Duarte, P.; Foces-Foces, C.; Cano, F. H.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1990**, 143−149. (c) Handa, M.; Mikuriya, M.; Zhong, Z. J.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3883−3887. (d) Tremel, W.; Kriege, M.; Krebs, B.; Henkel, G. *Inorg. Chem.* **1988**, *27*, 3886−3895. (e) Mikuriya, M.; Kida, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1180−1182. (f) Mikuriya, M.; Kida, S.; Ueno, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1987**, *58*, 1857−1858. (g) McKenzie C. J.; Robson, R. *Inorg. Chem.* **1987**, *26*, 3615. (h) Vance, T. B., Jr.; Wagner, L. G.; Seft, K. *Inorg. Chem.* **1977**, *16*, 2106−2109.

(7) (a) Yamamura, T.; Tadokoro, M.; Kuroda, R. *Chem. Lett.* **1989**, 1245−1246. (b) Yamamura, T.; Tadokoro, M.; Tanaka, K.; Kuroda, R. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1984−1990. (c) Fallon, G.; Gatehouse, B. M. *Acta Crystallogr.* **1976**, 97−101. (d) Marini, P.; Murray, K. S.; West, B. O. *J. Chem. Soc., Dalton Trans.* **1983**, 143. (e) Fallon, G.; Gatehouse, B. M.; Marini, P.; Murray, K. S.; West, B. O. *J. Chem. Soc., Dalton Trans.* **1984**, 2733. (f) Bertini, I.; Sacconi, L.; Speroni, G. P. *Inorg. Chem.* **1972**, *11*, 1323−1326.

(8) (a) Louey, M.; Nichols P. D.; Robson, R. *Inorg. Chim. Acta* **1980**, *47*, 87−96. (b) Robson, R. *Inorg. Chim. Acta* **1982**, *57*, 71−77. (c) Robson, R. *Inorg. Chim. Acta* **1984**, *85*, 195−198. (d) Crossley, T. E.; Hoskins, B. F.; McDonald I. A. S.; Robson, R. *Inorg. Chim. Acta* **1986**, *111*, 99−106. (e) Hoskins, B. F.; McKenzie, C. J.; Robson, R.; Zhenrong, L. *J. Chem. Soc., Dalton Trans.* **1990**, 2637−2641. (f) Iliopoulos, P.; Murray, K. S.; Robson, R.; Wilson, J. *J. Chem. Soc., Dalton Trans.*, **1987**, 1585−1591. (g) Brooker, S.; Croucher, P. D.; Roxburgh, F. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3031−3037.

(9) Sheldrick, G. M. SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467.

(10) Sheldrick, G. M. SHELXL-93. University of Göttingen, 1993.

Table 1. Crystal Data and Details of Structure Determinations

	[Ni(pftp)]	[Ni(peptp)]·CH_3CN	L^2Ni_2·$15H_2O$
empirical formula	$C_{21}H_{20}N_2NiO_2S_2$	$C_{37}H_{39}N_7NiS_2$	$C_{48}H_{82}N_8Ni_2O_{15}S_4$
formula weight	455.22	704.48	1256.88
crystal description	red-brown lath	orange plate	brown block
temperaure (K)	153(2)	153(2)	153(2) K
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$C2/c$
a (Å)	28.761(7)	10.247(7)	31.517(14)
b (Å)	8.582(2)	21.886(8)	8.980(2)
c (Å)	7.841(4)	15.662(9)	26.822(12)
β (deg)	98.92(3)	92.58(6)	117.17(2)
V (Å^3)	1912(1)	3509(3)	6754(5)
Z	4	4	4
density (calcd, Mg/m^3)	1.581	1.3343	1.236
μ (mm^{-1})	1.254	0.709	0.741
F(000)	944	1480	2664
crystal size (mm)	0.60 × 0.14 × 0.06	0.94 × 0.32 × 0.14	0.20 × 0.20 × 0.10
θ range for data collection (deg)	2.0 to 25.0	2.0 to 25.0	2.0 to 20.0
index ranges	$0 < h < 30$	$-1 < h < 12$	$0 < h < 30$
	$-1 < k < 9$	$-1 < k < 26$	$-1 < k < 8$
	$-8 < l < 8$	$-18 < l < 18$	$-25 < l < 22$
no. of reflns collected	1399	6849	3766
no. independent reflections	1204 ($R_{int} = 0.0347$)	6181 ($R_{int} = 0.034$)	3152 ($R_{int} = 0.0726$)
absorption correction	semiempirical (ψ scans)	semiempirical (ψ scans)	none
max and min transmission	0.924 and 0.825	0.768 and 0.701	
data/restraints/parameters	1204/0/129	6179/0/427	3152/5/192
goodness of fit on F^2 (all data)	1.071	1.024	0.944
final R indices [$I > 2\sigma(I)$]	R1 = 0.0383	R1 = 0.0544	R1 = 0.1359
	wR2 = 0.0710	wR2 = 0.1036	wR2 = 0.3559
R indices (all data)	R1 = 0.0635	R1 = 0.0999	R1 = 0.2468
	wR2 = 0.0794	wR2 = 0.1230	wR2 = 0.4023
largest peak and hole (e Å^{-3})	0.284 and −0.297	0.381 and −0.670	1.121 and −0.529

Table 2. Selected Bond Distances and Angles for Ni(pftp), Ni(peptp)·CH_3CN, and L^2Ni

	Ni(pftp)		
Ni−N(1)	1.907(4)	Ni−S(1)	2.1692(14)
N(1a)−Ni−N(1)[a]	90.7(2)	N(1)−Ni−S(1)	92.63(11)
N(1a)−Ni−S(1)	176.31(12)	S(1)−Ni−S(1a)[a]	84.07(7)
	Ni(peptp)·CH_3CN		
Ni−N(2)	1.904(3)	Ni−N(3)	1.913(4)
Ni−S(2)	2.171(2)	Ni−S(1)	2.1708(14)
N(2)−Ni−N(3)	90.3(2)	N(2)−Ni−S(2)	172.74(11)
N(3)−Ni−S(2)	93.93(11)	N(2)−Ni−S(1)	93.08(11)
N(3)−Ni−S(1)	173.14(11)	S(2)−Ni−S(1)	83.35(6)
	L^2Ni_2		
Ni−N(1)	1.94(2)	Ni−N(2)	1.97(2)
Ni−S(1)	2.178(8)	Ni−S(2)	2.188(8)
N(1)−Ni−N(2)	91.2(9)	N(1)−Ni−S(1)	94.9(6)
N(2)−Ni−S(1)	169.9(7)	N(1)−Ni−S(2)	172.1(7)
N(2)−Ni−S(2)	91.6(6)	S(1)−Ni−S(2)	83.4(3)

[a] (a): $-x + 1, y, -z + {}^1/_2$.

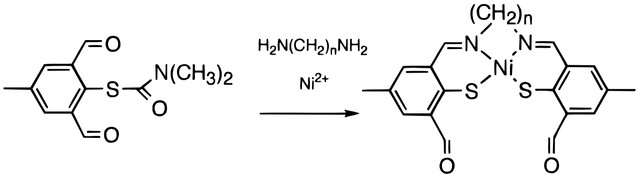


Figure 1. Ni(eftp), $n = 2$; Ni(pftp), $n = 3$.

their limited solubilty, it was possible to obtain ^{1}H NMR spectra for both Ni(eftp) and Ni(pftp) and a ^{13}C NMR spectrum for the slightly more soluble Ni(pftp). The signals for the hydrogen atom and the carbon atom of the unreacted aldehyde group of Ni(pftp) are observed at 10.85 and 193.66 ppm, respectively. In accordance with the square planar geometry about the nickel ion found in the crystal structure, *vide infra*, NMR spectra indicate that the complexes are low spin and diamagnetic. The strongest band in the IR spectra is at 1675 cm^{-1} and is assigned to $\nu_{C=O}$. The UV−visible spectrum of Ni(pftp) shows four bands. The spectrum of Ni(eftp) is similar apart from a shoulder at 492 nm. The features at approximately 600 nm (ϵ = ca. 300 M^{-1} cm^{-1}) in the ligand field region are assigned to a $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. The shoulder at 492 nm ($\epsilon = 1224$ M^{-1} cm^{-1}) in the spectrum of Ni(eftp) is assigned to a $^1A_{1g} \rightarrow {}^1B_{1g}$ transition. The extinction for this transition is high due to the fact that it overlaps with the strong band at approximately 460 nm assigned to the $S_\pi \rightarrow M$ charge transfer which is observed for both complexes. The second d−d transition in Ni(pftp) is presumably obscured by this CT band. The bands at 385 and 399 nm for Ni(eftp) and Ni(pftp) are assigned to a $S_\sigma \rightarrow M$ charge transfer.

The presence of two aldehyde groups in Ni(pftp)and Ni(eftp) makes these complexes obvious candidates for further derivation. We report here an initial exploration into the condensation reactions of these aldehyde groups with amines. Due to the slightly better solubility of Ni(pftp) compared to Ni(eftp) we have concentrated on utilizing this complex as a building block for other dithiophenolate-containing complexes. A particular goal is the preparation of unsymmetrical complexes such as those in Figure 2, where X might contain coordinating atoms appropriate for a second, and possibly different, metal ion. A comparable approach has been used previously with phenolate-based acyclic and macrocyclic ligands.[11] Figure 2a depicts a dinuclear complex of an acyclic ligand with two different metal-binding cavities and Figure 2b a dinuclear complex of an unsymmetrical compartmental macrocyclic ligand.

On the route to dimetallic complexes of the type in Figure 2a, the Schiff base condensation reaction of the aldehyde groups

---

(11) (a) Fraser, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 338−346. (b) McCollum, D. G.; Fraser, C.; Ostrander, R.; Rheingold, A. L.; Bosnich, B. *Inorg. Chem.* **1995**, *33*, 23832392. (c) Ohtsuka, S.; Kodera, M.; Motoda, K.; Ohba, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2637.

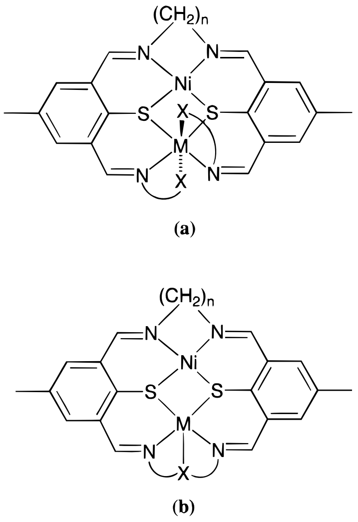
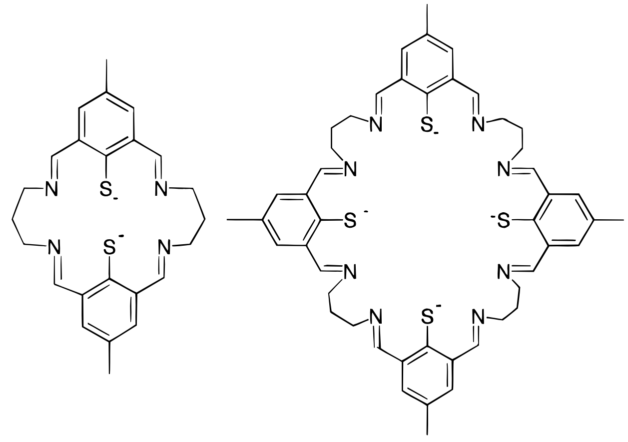


Figure 2. Proposed asymmetric dinuclear complexes using the dialdehyde building blocks Ni(eftp) ($n = 2$) and Ni(pftp) ($n = 3$). The dinuclear complex of (a) an acyclic system and (b) a compartmental macrocyclic ligand, obtained by the Schiff base condensation with appropriate amine-containing moieties (X). For one of the complexes described here, $[L^1Ni_2](ClO_4)_2$, $n = 3$ and $X = (CH_2)_3$ in (b) applies.



L^1 **L^2**

Figure 3. The 2 + 2 macrocycle, L^1 and 4 + 4 macrocycle, L^2.

of Ni(pftp) with the amine groups of two 2-(2-aminoethyl)-pyridines was carried out. The resulting diamagnetic nickel complex, [*N,N*-propane-1,3-diyl(6-(N-(2-ethylpyridyl)imino-methyl)-4-methyl-2-methyliminatothiophenolato)]nickel(II) (Ni-(peptp)) was isolated as a brown crystalline product. The structure of Ni(peptp) is described below. The spectroscopic features of Ni(peptp) are similar to its parent, Ni(pftp). The use of Ni(peptp) as a (metal-containing) ligand for a second metal ion to give the thiolate-bridged heterodinuclear complexes, $[(peptp)NiM]^{n+}$ will be the subject of ongoing work.

The Schiff base condensation reaction of Ni(pftp) with 1,3-diaminopropane gave the dinickel complexes of two different macrocycles; a 2 + 2 macrocycle, L^1 (formally the 2 + 2 condensation product of thiocresolato-2,6-dicarboxaldehyde and 1,3-diaminopropane), and the 4 + 4 macrocycle, L^2 (formally the 4 + 4 condensation product of thiocresolato-2,6-dicarboxaldehyde and 1,3-diaminopropane), shown in Figure 3.

The dithiophenolate-bridged macrocyclic complex [(10,23-dimethyl-13,26-dimercapto-2,6,15,19-tetraaza-1,7,14,20-tetraene-[7.7.7.7]metacyclophane)dinickel]diperchlorate ($[L^1Ni_2](ClO_4)_2$), was prepared by reaction of Ni(pftp) with 1 equiv of Ni^{2+} and of 1,3-diaminopropane in methanol/DMF. Elemental analysis and mass spectrometric results confirm the formulation of this previously reported[12] complex. The red crystals of $[L^1Ni_2](ClO_4)_2$ were suitable for X-ray analysis; however, this was not carried out since the structure of $[L^1Ni_2](ClO_4)_2{\cdot}2DMF$ has been determined by Atkins *et al.*[12] The preparation used by these workers is different from ours; they used a template Schiff base condensation of 2,6-diformyl-4-methylbenzenethiol and 1,3-diaminopropane in acetonitrile. The structure of $[L^1Ni_2](ClO_4)_2{\cdot}2DMF$[12] shows that the geometry around the hinging sulfur atoms is pyrimidal and that a consequence of this is that the dithiophenolate-bridged dinickel cation is V-shaped with the metal coordination planes tilted toward each other. The angle between the planes defined by the two planes of ligating atoms (N_2S_2 planes) is 144.4°. The Ni···Ni interatomic distance is 3.163(4) Å. The metal−metal separations are similar in the analogous diphenolate-bridged dinuclear complexes of Robson-type macrocycles; however, in contrast, these complexes are essentially planar due to the planar geometry of the hinging oxygen atoms.[13]

Using similar synthetic routes involving reaction of Ni(pftp) with a second metal ion, we are presently working on the preparation of heterodinuclear complexes analogous to $[L^1Ni_2](ClO_4)_2$ (Figure 2b, $M \neq Ni$, $X = (CH_2)_3$). The initial investigations of the reaction of Ni(pftp) with diamines and a metal ion (Zn^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Pd^{2+}, Cd^{2+}) have on a few occasions yielded solid products; however, further work is necessary for their characterization.

The reaction of Ni(pftp) with 1,3-diaminopropane carried out in acetonitrile in the presence of $PdCl_2$ gave the fascinating result of a dinickel complex of the novel 4 + 4 macrocycle in Figure 3. Crystals of L^2Ni_2 (L^2 = (10,23,36,49-tetramethyl-13,26,-39,52-tetramercapto-2,6,15,19,28,32,41,45-octaaza-1,7,14,20,-27,33,40,46-octaene[7.7.7.7]metacyclophane) were isolated in a small yield. The brown flaky crystals were of poor quality; nevertheless, it was possible to confirm the structural arrangement by X-ray crystallography. The FAB mass spectrum of L^2Ni_2 shows a peak cluster centered at *m/z* 985, with an isotopic pattern appropriate for the protonated molecular ion. Sufficient quantities of L^2Ni_2 for a full spectroscopic and analytical characterization have not been obtained. We are working on the optimization of the synthesis of L^2Ni_2 with the expectation that work with this macrocycle may lead to a rich coordination chemistry with, in particular, the "soft" metal ions. Clearly, the reaction of L^2Ni_2 with other metal ions is a plausible route to novel heterotetranuclear complexes with a $[L^2Ni_2M_2]^{n+}$ formulation. L^2Ni_2 represents a rare example of a complex of a Schiff base macrocycle derived from the condensation of more than four subunits (as in the more common 2 + 2 macrocycles). A hexanuclear copper complex of a 3 + 3 macrocycle[14] and a tetranickel complex of a 4 + 4 macrocycle[15] have been described. Both systems comprise phenolate head groups. The syntheses of these 3 + 3 and 4 + 4 macrocyclic complexes require the self-assembly of six organic subunits and six metal ions, and eight organic subunits and four metal ions, respectively in a "one-pot" reaction. By contrast, the preparation of L^2Ni_2 is formally a 2 + 2 condensation of preprepared Ni(pftp) and 1,3-diaminopropane. Thus, the build-up of the 4 + 4 macrocycle, L^2, involves two discrete steps.

---

(12) Atkins, A. J.; Blake A. J.; Schröder, M. *J. Chem. Soc., Chem Commun.* **1993**, 1662.

(13) Hoskins, B. F.; Robson, R. R.; Williams, G. A. *Inorg. Chim. Acta* **1976**, *16*, 121.

(14) (a) Hoskins, B. F.; Robson, R. R.; Smith, P. *J. Chem. Soc., Chem Commun.* **1990**, 488. (b) Tandon, S. S.; Thompson, L. K.; Brisdon, J. N. *Inorg. Chem.* **1995**, *34*, 5507.

(15) (a) Brooker, S.; McKee, V.; Shepard, W. B.; Pannell, L. K. *J. Chem. Soc., Dalton Trans.* **1987**, 2555. (b) Nanda, K. K.; Venkatsubramanian, K.; Majumdar, D.; Nag, K. *Inorg.Chem.* **1994**, *33*, 1581.

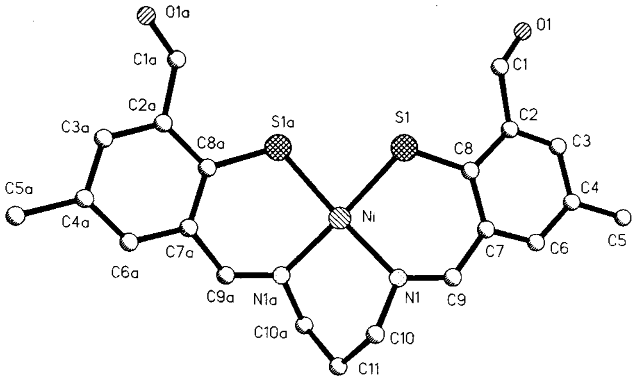


Figure 4. Molecular structure of Ni(pftp) showing the numbering scheme.

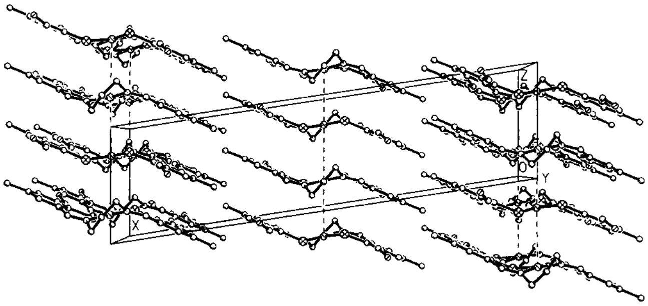


Figure 5. Packing diagram for Ni(pftp) parallel to the *z* axis.

Crystal Structures. Ni(pftp). Diffraction-quality crystals were obtained directly from the reaction mixture. The structure of the asymmetric unit is shown in Figure 4. The ligand, pftp, binds one nickel ion at the N_2S_2 site. A crystallographic twofold axis bisects the complex, passing through both the Ni atom and C11. The geometry at Ni is approximately square planar but the molecule as a whole has a chair conformation; each phenyl ring makes an angle of 35.3(1)° with the N_2S_2 plane. The deviations of the coordinating atoms from the least square plane made up of NiS_2N_2 are not greater than 0.029(2) Å, showing that the coordination around the Ni atom is relatively planar. The packing diagram (Figure 5) shows the molecules stacked parallel to the *z* axis with the nickel atoms aligned directly above one another and 3.96 Å apart. The interplanar distance between adjacent phenyl rings is 3.57 Å, slightly longer than the normal $\pi-\pi$ stacking distance of ca 3.4 Å. Similarly to the crystal structure of Ni(tsalen)[5a,b] the molecules are paired. There is no evidence for an axial interaction between the Ni atom in one molecule with a sulfur atom in an adjacent molecule (Ni-(molecule a)···S(molecule b), 4.070 and 4.538 Å). In fact, the intermolecular Ni(molecule a)···Ni(molecule b) separation is closer at 3.961 Å. These features contrast with the structure of Co(tsalen)[5c] in which the coordination around cobalt is best described as square pyramidal, in which the Co interacts axially with a sulfur atom on the adjacent molecule (Co···2.444(1) Å).

Ni(peptp). The asymmetric unit contains one molecule of Ni(peptp) and an acetonitrile solvate molecule (Figure 6). There are no significant interactions of the acetonitrile molecule with the complex molecule. The nickel ion is coordinated to both thiophenolate sulfur atoms and to the two imine nitrogen atoms on the "closed" side of the ligand. The Ni coordination geometry is approximately square planar, although there is a twist of 8.4(2)° between the two (N, S, Ni) planes. The two thiophenolate rings are approximately parallel but not coplanar, their respective planes being ca. 1.4 Å apart. The mean plane of the Ni donors is at 30.9(1) and 30.2(1)° to the thiophenolates containing S1 and S2, respectively. The pyridine pendant arms are interwoven with those of neighboring molecules, but surprisingly, they are not involved in any $\pi-\pi$ interactions. The only such interaction involves the thiophenol−diimine systems of adjacent complexes, which are separated by ca. 3.4 Å.

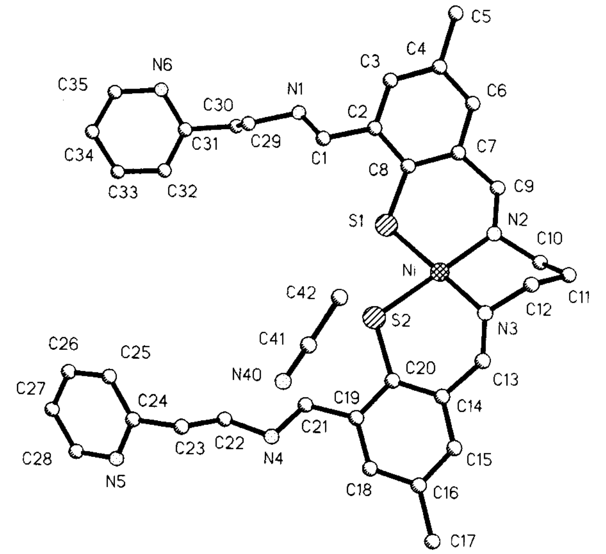


Figure 6. Molecular structure of Ni(peptp) showing the numbering scheme.

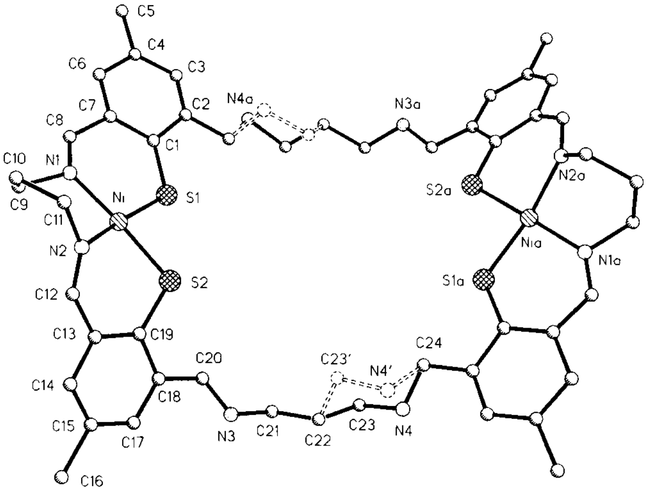


Figure 7. Molecular structure of L^2Ni_2 showing the numbering scheme.

L^2Ni_2. The poor quality of the X-ray data obtained for L^2Ni_2 means that, although the structure of the complex has been established, the nature and number of solvate molecules is still unclear and the refinement is not good. The structure of L^2Ni_2 (Figure 7) can be likened to two Ni(pftp) complexes linked by two propylenediamine units. The complex is bowl shaped with angle of 77° between the two planes of the Ni donor sets; the interatomic Ni···Ni distance is 11.4 Å. This complex is a potentially interesting host for the binding of guest molecules within the large cavity.

Conclusions

The two aldehyde functionalities, Ni(eftp) and Ni(pftp), react with amines to furnish complexes of dithiophenolate-containing Schiff base ligands. Using this method, an acyclic system, Ni-(peptp), and the dinickel complexes of a 2 + 2 and the novel 4 + 4 macrocycle, $[L^1Ni_2](ClO_4)_2$ and L^2Ni_2, were obtained. In $[L^1Ni_2](ClO_4)$, the thiolate sulfur atoms of the macrocroycle L^1 bridge the two metal centers. The synthons and synthetic routes described here may offer a possibility for facile preparation of multinuclear homo- and heteronuclear complexes of thiophenolate-containing ligands. Specifically, the presence of an iron atom as M in an unsymmetrical complex of the type depicted by Figure 2 would be interesting as a model compound for the active site of hydrogenase. As well as hampering investigations into the reactivity of the present series of nickel complexes, their general insolubility has hindered a more extensive spectroscopic and physical characterization and, in particular, electrochemical characterization. This outcome is disappointing with respect to the aim of characterization of useful spectroscopic models for cysteine-bound metal ions. We are presently working on the incorporation of solubilizing groups on the ligand backbones in the hope of circumventing these solubility problems. It is our intention to continue this work in the persuit of mixed metal complexes of three of the new ligands reported here, peptp, L^1, and L^2, i.e., complexes of the general formulation $[(\text{peptp})\text{NiM}]^{n+}$, $[L^1\text{NiM}]^{n+}$, and $[L^2\text{Ni}_2\text{M}_2]^{n+}$.

Acknowledgment. C.J.McK. is grateful to the Danish Research Council (No. 9503162) and V.McK. to the EPSRC for support.

Supporting Information Available: Atomic coordinates, thermal parameters, full listings of bond distances and angles and H-atom coordinates (13 pages). Ordering information is given on any current masthead page.

IC970713R