CHEMCOMM
Communication
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The effect of *N*-methylation on the chemical reactivity of binuclear Ni amine-thiophenolate complexes†

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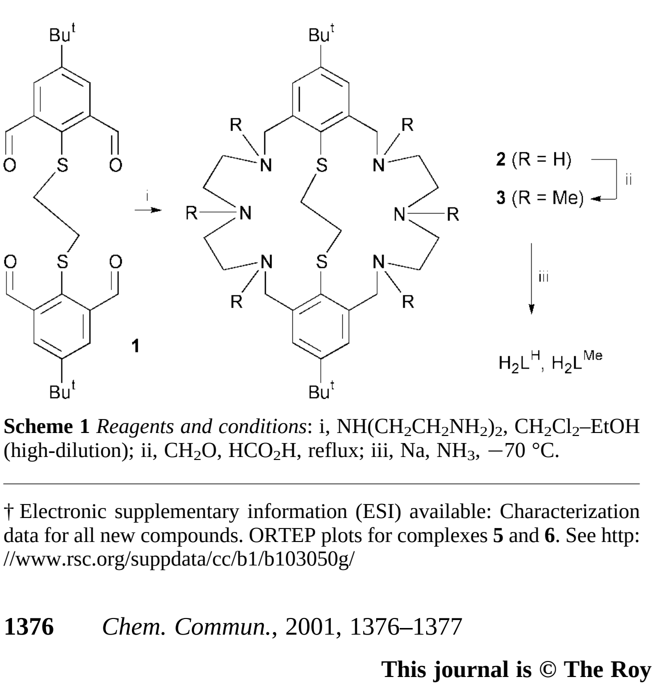
Received (in Cambridge, UK) 4th April 2001, Accepted 20th June 2001
First published as an Advance Article on the web 6th July 2001

Macrocyclic amine thiophenolate ligands are shown to form face-sharing bioctahedral nickel complexes with a central $N_3Ni(\mu\text{-}SR)_2(\mu\text{-}Cl)NiN_3$ core structure. The bridging halide ion can be readily replaced when all six nitrogen atoms are tertiary amine donors.

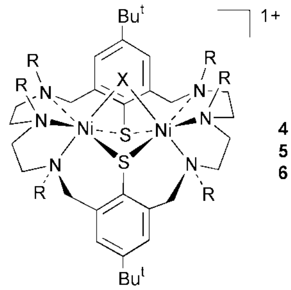
Thiolate complexes of first row transition metals are generally labile and it is therefore difficult to control their chemical reactivity. This is true in particular for binuclear species.[1,2] For systematic investigations, complexes of macrocyclic thiophenolate ligands seem to be ideal, because of their greater thermodynamic stability and proper positioning of free coordination sites for substrate binding. However, traditional routes developed for the corresponding phenolate macrocycles[3] fail for the synthesis of sensitive thiophenolates. This situation has changed greatly in the last few years due to the work by the groups of Brooker,[4] McKee[5] and Schröder[6] who have used (*S*)-(2,6-diformyl-4-methylphenyl)dimethylthiocarbamate as thiophenolate precursor in metal templated Schiff-base condensation reactions with α,ω-diamines. The resulting thiophenolate macrocycles bear additional imine, secondary amine, and even hydroxy groups in the linking side arms. However, it has not been possible to access derivatives with tertiary amine functions. We describe here the syntheses, X-ray crystal structures and properties of binuclear Ni complexes of such ligands.

Macrocycle **2** was obtained by a [2 + 1] condensation reaction between tetraaldehyde **1**[7] and bis(aminoethyl)amine in an ethanol–dichloromethane mixed solvent system using medium-dilution conditions followed by reduction with $NaBH_4$ (Scheme 1). The yields of the new bicyclic amine-thioether are excellent (>90%). An attractive feature of **2** compared to unprotected thiolate ligands is that its secondary amines are readily alkylated without affecting the masked thiolate functions. Thus, reductive methylation of **2** with formaldehyde and formic acid under Eschweiler–Clarke conditions gave the permethylated derivative **3** in nearly quantitative yield. Compound **3** displays only twelve resonances in its ^{13}C NMR spectrum ruling out the possibility that it exists as a mixture of conformationally stable isomers. Both the unmethylated and the permethylated thioether could be converted to the corresponding thiophenols H_2L^H and H_2L^{Me} by using sodium in liquid ammonia as reducing agent.



Scheme 1 *Reagents and conditions*: i, $NH(CH_2CH_2NH_2)_2$, CH_2Cl_2–EtOH (high-dilution); ii, CH_2O, HCO_2H, reflux; iii, Na, NH_3, −70 °C.

The reaction of $NiCl_2\cdot 6H_2O$ with $H_2L^H\cdot 6HCl$ in methanol using NEt_3 as base (2 : 1 : 8 molar ratio) was found to produce the green, air-stable complex $[(L^H)Ni^{II}_2(\mu\text{-}Cl)]^{1+}$ **4**. The cation was isolated as the perchlorate salt **4**·ClO_4 in 80% yield. Crystallographic characterization of **4**·ClO_4,‡ using crystals obtained by recrystallization from methanol, confirmed the structure of **4** to consist of a confacial bioctahedral species (Fig. 1). The coligand is found in a bridging position. In the context of coordinatively unsaturated Ni thiolate complexes, the presence of a bridging halide ligand in **4** is without precedent. Most binuclear



4 (R = H, X = Cl)
5 (R = Me, X = Cl)
6 (R = Me, X = OH)

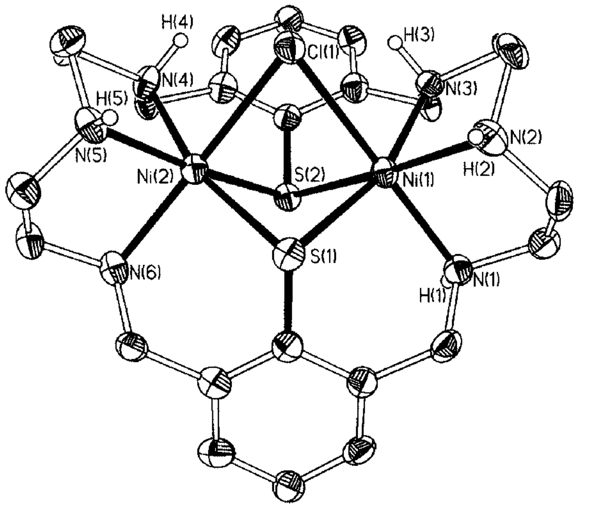


Fig. 1 Structure of the μ-Cl complex **4** with thermal ellipsoids drawn at the 50% probability level. *tert*-Butyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths. Values in square brackets represent bond lengths for **5**. (Å): Ni(1)–Cl(1) 2.639(2) [2.433(2)], Ni(1)–S(1) 2.418(2) [2.471(2)], Ni(1)–S(2) 2.419(2) [2.405(2)], Ni(1)–N(1) 2.078(6) [2.352(5)], Ni(1)–N(2) 2.103(7) [2.173(5)], Ni(1)–N(3) 2.085(6) [2.181(5)], Ni(2)–Cl(1) 2.602(2) [2.450(2)], Ni(2)–S(1) 2.423(2) [2.498(2)], Ni(2)–S(2) 2.405(2) [2.423(2)], Ni(2)–N(4) 2.099(7) [2.171(5)], Ni(2)–N(5) 2.141(7) [2.175(6)], Ni(2)–N(6) 2.134(7) [2.380(6)]; Ni···Ni 3.098(2) [3.184(2)].

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† Electronic supplementary information (ESI) available: Characterization data for all new compounds. ORTEP plots for complexes **5** and **6**. See http://www.rsc.org/suppdata/cc/b1/b103050g/

DOI: 10.1039/b103050g

complexes feature a dithiolate bridged Ni(μ-SR)$_2$Ni core structure.[4–6] However, all attempts to replace the halide substituent in **4** have failed so far.

On these grounds, we synthesized the complex [(L^{Me})Ni$^{II}_2$(μ-Cl)]$^{1+}$ **5** by using reaction conditions similar to those described above for **4**. It was isolated as the yellow microcrystalline perchlorate salt **5**·ClO$_4$ in 85% yield. Electronic absorption spectroscopy (ESI†) and X-ray crystal structure determination‡ provided new insights into the coordination chemistry of the permethylated amine-thiolate ligand H$_2$L^{Me}. Two bands assigned as ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$, splitting due to lower symmetry) are observed at 920 and 1002 nm in the UV–VIS spectrum of **5**·ClO$_4$. Compared to **4** (894 and 941 nm) these bands are shifted to lower energies indicative of a significantly weaker ligand field strength of H$_2$L^{Me}. The crystal structure determination of **5**·BPh$_4$‡ revealed the structure of the μ-chloro complex **5** to be very similar to **4**. The structure of **5** may be simply derived from that of **4** by replacing the six NH hydrogen atoms by methyl groups. The conversion of secondary into tertiary amines results in an increase of the average Ni–N bond length by 0.139 Å, which in turn results in a decrease of the average Ni–Cl distance by 0.178 Å. Similar effects have also been observed for nickel complexes of other azamacrocycles and their methylated derivatives.[8]

Preliminary binding studies demonstrate that utilization of the permethylated ligand H$_2$L^{Me} in place of H$_2$L^H drastically alters the ease of substitution of the bridging halide substituent, presumably because of the more hydrophobic microenvironment about the μ-Cl function in **5**. Thus, while the latter reacts with NBu$^n_4$OH in acetonitrile to produce the μ-OH complex **6**, complex **4** was found to be unreactive. Even the addition of a halide scavenger such as Pb^{II}(ClO$_4$)$_2$ did not lead to substitution of the Cl$^-$ ion.

A crystallographic analysis of **6**·BPh$_4$‡ revealed **6** to be isostructural with **5**. The OH group replaces the μ-Cl ligand, demonstrating that the substitution reaction takes place without gross structural changes of the parent complex. The average Ni–O bond length at 2.10 Å is typical for hydroxide-bridged dinickel centers.[9] The Ni–N and Ni–S bond lengths are similar to those in **5**, however, the separation of the Ni atoms has decreased to 3.037(3) Å. It is also worth mentioning that the OH unit [ν(OH) = 3543 cm^{-1}] is not involved in hydrogen bonding interactions.

Cyclic voltammetry experiments have shown that **4**·ClO$_4$ undergoes two one-electron oxidations at $E^1_{1/2}$ = +0.27 V [≡ $E_{1/2}$(Ni^{III}Ni^{II}/Ni^{II}Ni^{II}), ΔE_p = 91 mV] and at $E^2_{1/2}$ = 1.05 V [≡ $E_{1/2}$(Ni^{III}Ni^{III}/Ni^{III}Ni^{II}), irrev.] *vs.* SCE. The cyclic voltammogram of **5**·ClO$_4$ is very similar, but this complex is oxidized at more positive potentials at $E^1_{1/2}$ = +0.43 V (85 mV) and at $E^2_{1/2}$ = +1.37 V (irrev.) *vs.* SCE. The first oxidation of complex **6**·BPh$_4$, on the other hand, occurs at less positive potentials [$E^1_{1/2}$ = +0.26 V (94 mV); the value for $E^2_{1/2}$ could not be determined due to oxidation of the BPh$_4^-$ anion; a ClO$_4^-$ salt of **6** could not be obtained in a pure form]. The shifts of the redox potentials can be explained by the different coordination environments about the Ni ions. Tertiary amine donors exert weaker ligand fields than secondary amine functions. Complex **5** is thus more difficult to oxidize than **4**. The OH ligand in **6**, on the other hand, exerts a stronger ligand field than the halide ion in **5** and the former complex is thus more easily oxidized. Remarkably, all Ni^{III}Ni^{III} species are not stable on the time-scale of a cyclic voltammetry experiment. This is in marked contrast to the behavior of coordinatively saturated Ni amine-thiolate complexes,[10] which can be reversibly oxidized to Ni^{III}Ni^{III} species. It is assumed that the different electrochemical properties are due to redox transformations of the bridging coligand or decomposition reactions of the Ni^{III} species.

In summary, the macrocyclic amine-thiolate ligand H$_2$L^H gives rise to an unprecedented type of coordinatively unsaturated amine-thiolate complex. The use of H$_2$L^{Me} in place of H$_2$L^H facilitates rapid substitution reactions at the bridging position, which encourages further exploration of the chemical reactivity of complex **5** and its derivatives.

This research was supported by the Deutsche Forschungsgemeinschaft. We thank Professor Dr H. Vahrenkamp for his generous support of this work.

Notes and references

‡ *Crystal data* for **4**·ClO$_4$·MeOH: $C_{33}H_{56}Cl_2N_6Ni_2O_5S_2$, M_r = 869.28, orthorhombic, space group *Iba*2 (no. 45), T = 293(2) K, μ(Mo-Kα) = 0.22 mm^{-1}, a = 23.941(5), b = 26.974(5), c = 12.477(2) Å, V = 8058(3) Å^3, Z = 8. 25074 measured reflections, 8935 were unique (R_{int} = 0.1201), R_1, wR_2 = 0.0587, 0.1289 [$I > 2\sigma(I)$]. For **5**·BPh$_4$·MeOH: $C_{63}H_{88}BClN_6Ni_2OS_2$, M_r = 1173.19, triclinic, space group $P\bar{1}$ (no. 2), T = 180(2) K, μ(Mo-Kα) = 0.754 mm^{-1}, a = 14.668(3), b = 20.140(4), c = 22.960(5) Å, α = 87.65(3), β = 80.96(3), γ = 69.39(3)°, V = 6269.0(22) Å^3, Z = 4. 55881 measured reflections, 28884 were unique (R_{int} = 0.0557), R_1, wR_2 = 0.0674, 0.1933 [$I > 2\sigma(I)$]. For **6**·BPh$_4$·MeOH: $C_{63}H_{89}BN_6Ni_2O_2S_2$, M_r = 1154.75, triclinic, space group $P\bar{1}$ (no. 2), T = 180(2) K, μ(Mo-Kα) = 0.672 mm^{-1}, a = 13.734(3, b = 14.093(3) Å, c = 18.094(4) Å, α = 103.24(3)°, β = 97.42(3), γ = 98.09(3)°, V = 3327.5(13) Å^3, Z = 2. 30866 measured reflections, 15786 were unique (R_{int} = 0.0959), R_1, wR_2 = 0.0893, 0.2381 [$I > 2\sigma(I)$]. The structures were determined by direct methods in SHELXS-86, refinements were carried out with SHELXL-93.[11]

CCDC reference numbers 162721–162723. See http://www.rsc.org/suppdata/cc/b1/b103050g/ for crystallographic data in CIF or other electronic format.

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