Novel Trinuclear and Dinuclear Nickel Coordination Compounds with a New Pentadentate Ligand. Crystal Structures of $[Ni_3(bdnol)(EtOH)Cl_5]$ and $[Ni_2(bdnol)Cl_3]$

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The pentadentate ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonan-5-ol (Hbdnol) yields, with nickel chloride, the unique trinuclear compound $[Ni_3(bdnol)(EtOH)Cl_5]$ with two $[NiNSOCl_3]$ and one $[NiCl_4OO']$ distorted octahedral chromophores, and the dinuclear compound $[Ni_2(bdnol)Cl_3]$, with two $[NiNSOCl_2]$ distorted trigonal bipyramidal chromophores.

In the last decade, the biological significance of nickel has been recognized.[1] Nickel appears to be an important metal in several classes of enzymes, notably in hydrogenases. EPR measurements and EXAFS data suggest that the nickel containing hydrogenases share a common nickel active site, in which the nickel ion is believed to be in a distorted octahedral or square pyramidal geometry, surrounded by sulfur, oxygen and/or nitrogen donor atoms. Some controversy still exists about the oxidation states of the nickel ion in the catalytic cycle.[1,2]

The ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol (Hbdnol), a pentadentate ligand with two azole ntirogens, two thioether sulfurs and an alcohol function has been designed and successfully synthesized by us.† The ligand was meant to form mononuclear, square-planar or five-coordinated nickel compounds, so that at least one open site for substrate coordination would remain available. However, reaction of Hbdnol with nickel chloride in ethanol with the addition of triethylformate (for dehydration) yields a green compound with the unusual formula $[Ni_3(bdnol)(EtOH)Cl_5]\cdot3EtOH$, **1**·3EtOH). When the reaction is performed in acetonitrile a red compound is obtained instead, with the formula $[Ni_2(bdnol)Cl_3]\cdot MeCN$, (**2**·MeCN). With nickel bromide only the red, dinuclear compound could be successfully prepared. The compounds have been characterized by elemental analysis‡ and spectroscopic techniques. The ligand field spectra of either compound could not be interpreted straightforwardly. Compound **2** appeared to be high spin, with LF maxima at 20.7, 18.6, 11.7, 10.3 and 7.6×10^3 cm^{-1}, so that a square-planar coordination was ruled out. A five-coordination, in which the apparently dehydronated alcohol group and one of the chloride ions are bridging the two nickel ions, was considered to be the most likely.[3] The green

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† The ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol was prepared from *N*-(2-mercaptoethyl)pyrazole and 1,3-dichloropropan-2-ol in a procedure that will be published elsewhere (E. Bouwman, P. Evans, R. A. G. de Graaff, H. Kooijman, J. Reedijk and A. L. Spek, manuscript in preparation).

‡ Satisfactory elemental analyses were obtained for **1**·2EtOH and **2**·$\frac{1}{2}$MeCN. The different number of solvent molecules, compared with the crystal structures, is accounted for by solvent loss.

compound **1** shows a rather irregular but apparently octahedral spectrum (LF maxima at 23.9, 21.9, 13.1 and 9.1 × 10^3 cm^{-1}); this observation could only be interpreted after the structure determination. Also, the stoichiometry of three nickel ions to one ligand appeared to be quite unusual. The crystal structures of both compounds finally gave insight in the composition of both the green **1**§ and the red **2**§ compound.

A projection of the unique structure of complex **1** is depicted in Fig. 1. The asymmetric unit contains a molecule of [Ni_3(bdnol)(EtOH)Cl_5] and three disordered ethanol molecules. All three nickel ions are bridged by the alkoxide group of the pentadentate ligand, with approximately the same nickel to oxygen distances of about 2.04 Å. The three nickel ions form an equilateral triangle, with all nickel to nickel distances being only 3.0 Å. The Ni–O–Ni angles are all *ca.* 96°, which is quite small. Of the five chloride ions, one is μ_3-bridging to all three nickel ions (Ni–Cl 2.47–2.59 Å), three are μ_2-bridging (Ni–Cl 2.40–2.52 Å) and one is terminally coordinated (Ni–Cl 2.32 Å). Two of the nickel ions [Ni(1) and Ni(2)] are nearly equivalent and are coordinated in an $NSOCl_3$ chromophore. The three donor atoms from the ligand are folded around the nickel ions in a meridional fashion. The bond distances are normal for divalent nickel ions in an octahedral geometry. The third nickel ion Ni(3) is distinct and is coordinated in a *trans* Cl_4O_2 chromophore, it is bound to the alkoxide oxygen and four of the chloride ions; the sixth coordination site is occupied by the ethanol molecule. The octahedral geometries of all three nickel ions are severely distorted; the bond angles around Ni are in the range of 82 to 110°.

A projection of the structure of complex **2** is given in Fig. 2. The asymmetric unit contains a molecule of [Ni_2(bdnol)Cl_3] and a non-coordinating acetonitrile molecule. A non-crystallographic mirror plane is running through C15, O20 and Cl2, perpendicular to the nickel–nickel vector. The two nickel ions are bridged by the dehydronated alcohol group of the ligand and one of the chloride ions. The nickel to nickel distance is 3.26 Å, and the Ni–O–Ni angle is relatively large (113.2°), especially when compared with **1**. Similar large angles, however, have been observed before.[4] Both nickel ions are in a five-coordination with an $NSOCl_2$ chromophore.

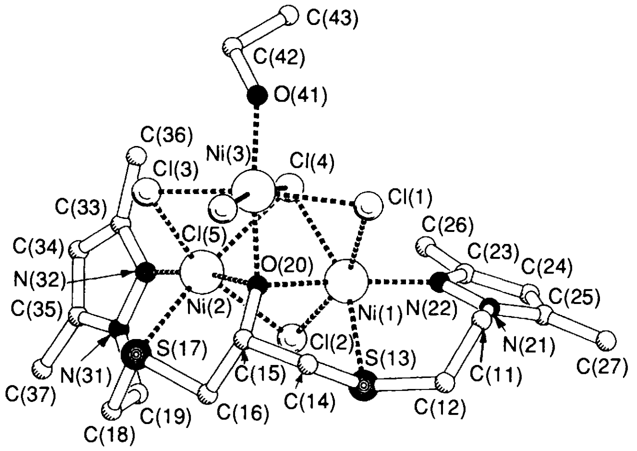

Fig. 1 Crystal structure of **1**. Hydrogen atoms and the solvent molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ni(1)–Ni(2) 3.061(2), Ni(1)–Ni(3) 3.071(2), Ni(2)–Ni(3) 3.027(2), Ni(1)–Cl(1) 2.483(1), Ni(1)–Cl(2) 2.430(1), Ni(1)–Cl(4) 2.474(1), Ni(1)–S(13) 2.394(1), Ni(1)–O(20) 2.038(3), Ni(1)–N(22) 2.032(4), Ni(2)–Cl(2) 2.516(1), Ni(2)–Cl(3) 2.411(1), Ni(2)–Cl(4) 2.517(1), Ni(2)–S(17) 2.386(1), Ni(2)–O(20) 2.038(3), Ni(2)–N(32) 2.019(3), Ni(3)–Cl(1) 2.399(1), Ni(3)–Cl(3) 2.397(1), Ni(3)–Cl(4) 2.593(1), Ni(3)–Cl(5) 2.326(1), Ni(3)–O(20) 2.059(4), Ni(3)–O(41) 2.017(4); Ni(1)–O(20)–Ni(2) 97.3(1), Ni(1)–O(20)–Ni(3) 97.0(1), Ni(2)–O(20)–Ni(3) 95.3(2), Ni(1)–Cl(4)–Ni(2) 75.60(4), Ni(1)–Cl(4)–Ni(3) 74.51(4), Ni(2)–Cl(4)–Ni(3), 72.64(3), Ni(1)–Cl(2)–Ni(2) 76.41(4), Ni(1)–Cl(1)–Ni(3) 77.89(4), Ni(2)–Cl(3)–Ni(3) 78.05(4), S(13)–Ni(1)–N(22) 90.0(1), S(13)–Ni(1)–O(20) 84.1(1), S(13)–Ni(1)–Cl(4) 160.27(5), O(20)–Ni(1)–N(22) 172.6(2), Cl(1)–Ni(1)–Cl(2) 161.90(5), Cl(1)–Ni(3)–Cl(3) 163.07(5), Cl(4)–Ni(3)–Cl(5) 172.24(5), O(20)–Ni(3)–O(41) 168.3(2)°.

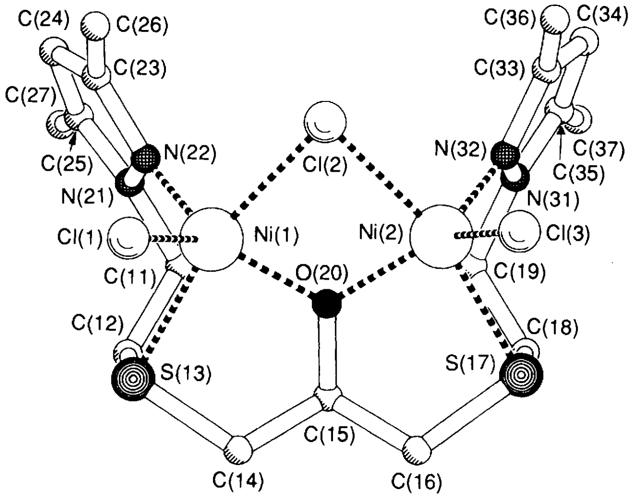

Fig. 2 Crystal structure of **2**. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ni(1)–Ni(2) 3.262(4), Ni(1)–Cl(1) 2.287(5), Ni(1)–Cl(2) 2.399(5), Ni(1)–S(13) 2.459(6), Ni(1)–O(20) 1.94(1), Ni(1)–N(22) 1.96(1), Ni(2)–Cl(2) 2.400(5), Ni(2)–Cl(3) 2.273(6), Ni(2)–S(17) 2.445(5), Ni(2)–O(20) 1.96(1), Ni(2)–N(32) 1.97(1); Ni(1)–O(20)–Ni(2) 113.2(5), Ni(1)–Cl(2)–Ni(2) 85.6(2), Cl(1)– Ni(1) –Cl(2) 97.2(2), Cl(1)–Ni(1)–S(13) 95.6(2), Cl(1)–Ni(1)–O(20) 131.6(3), Cl(1)–Ni(1)–N(22) 107.5(4), Cl(2)–Ni(1)–S(13) 164.0(2), Cl(2)–Ni(1)–O(20) 80.4(3), Cl(2)–Ni(1)–N(22) 93.7(3), S(13)–Ni(1)–O(20) 84.0(3), S(13)–Ni(1)–N(22) 91.5(3), O(20)–Ni(1)–N(22) 120.8(4)°.

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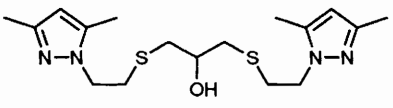
§ *Crystal data* for **1**·3EtOH: $C_{19}H_{33}Cl_5N_4Ni_3O_2S_2 \cdot 3C_2H_6O$, M_r = 905.17, yellowish plate crystal (0.025 × 0.20 × 0.45 mm), triclinic, space group $P\bar{1}$, a = 10.1243(3), b = 11.4308(6), c = 17.0088(6) Å, α = 73.042(4), β = 86.427(3), γ = 87.049(4)°, V = 1878.02(14) Å^3, Z = 2, D_c = 1.601 g cm^{-3}, 7148 reflections ($\theta < 25.4°$, $\omega/2\theta$ scan, T = 150 K) were measured on an Enraf Nonius CAD4 Turbo rotating anode diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lp and absorption (DIFABS; correction range 0.904–1.173). The structure was solved with DIRDIF92 and refined on F^2 with SHELXL-93 to $R1$ = 0.047 [5308 reflections with $F > 4\sigma(F)$] and $wR2$ = 0.127 [6888 reflections; 421 parameters]. H-atoms were taken into account at calculated positions. The molecules of crystallisation are disordered. No residual density outside −0.64 to 0.93 e Å^{-3}.

For **2**·MeCN: $C_{17}H_{27}Cl_3N_4Ni_2OS_2 \cdot C_2H_3N$, M_r = 632.35, red, poorly diffracting, plate shaped crystal (0.5 × 0.3 × 0.1 mm), monoclinic, space group $P2_1/c$ (no. 14) with a = 11.973(6), b = 8.140(6), c = 26.217(12) Å, β = 93.41(4)°, V = 2551(3) Å^3, Z = 4, D_c = 1.646 g cm^{-3}, $F(000)$ = 1304, μ(Mo-Kα) = 19.8 cm^{-1}, 7910 reflections measured, 5844 independent ($0.78 < \theta < 27.50°$, $\omega/2\theta$ scan, T = 150 K, Mo-Kα rdiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for L_p and for a linear decay of 9% of the reference reflections during 44 h of X-ray exposure time; empirical absorption correction applied (DIFABS, correction range 0.815–1.216). The structure was solved with DIRDIF92 and refined on F^2 with SHELXL-92. No observance criterium was applied during refinement. Refinement converged at a final $wR2$ value of 0.314, $R1$ = 0.132 [for 1873 reflections with $F_o > 4\sigma(F_o)$] S = 0.96 for 169 parameters. Hydrogen atoms were included in the refinement on calculated positions. The Ni, Cl and S atoms were refined with anisotropic thermal parameters; all other non-hydrogen atoms could only be refined with isotropic thermal parameters due to the poor quality of the crystal. A final difference fourier showed no residual density outside −1.15 and 1.19 e Å^{-3} (near Ni). Currently attempts are being undertaken to grow better crystals.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Hbdnol

The geometry of the nickel ions is intermediate between a square pyramidal and a trigonal bipyramidal geometry. In the case of a trigonal bipyramid, the axis can be considered to be running through the bridging chloride and the thioether sulfur (Cl–Ni–S 164°). For a square pyramid, the pyrazole nitrogen resides in the apical position. The ligand is folded around the nickel ion in a way different to that in the trinuclear complex: the N, S and O donor atom are now arranged in a facial conformation.

Reconsidering the unconventional trinuclear structure **1**, it can be regarded as being formed out of the dinuclear compound **2**, onto which an additional $NiCl_2$ unit is 'stuck', thereby inducing only a slight conformational change of the ligand. The ligand is more stretched out in the trinuclear compound and goes from a facial binding mode in **2** to a meridional binding mode in compound **1**. Nickel bromide only yields the dinuclear analogue, presumably because of steric effects: the trinuclear complex with four bridging halides is rather crowded. The analyses of both compounds already indicated that the ligand had to be dehydronated, although no base has been added to the reaction mixtures. Spontaneous dehydronation has been observed for phenol-type ligands,[5] but usually addition of a base is needed,[4,6] especially in the case of aliphatic hydroxides.[7]

μ_3-Alkoxide bridges usually result in cubane-type clusters: early examples are given by hydroxide[8] and methoxide[9] bridged cubanes. Also, cubane compounds with chelating ligands such as aminoethanolate[10] and pyrazolemethanolate[11] have been reported. Chelating ligands with an aliphatic alcohol group are reported only as Schiff base type ligands (L), which form nickel complexes either with formula $[Ni_2(L^{3-})X]$, or with formula $[Ni(L^{2-})]$, in which the alcohol group is not dehydronated and non-coordinating; in both complexes the nickel ions are in a square planar geometry.[7]

Further studies dealing with the electrochemical behaviour of the nickel compounds and magnetic susceptibility measurements are ongoing.

The research of E. B. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences. P. E. (University of East Anglia, Norwich) was involved in the project through the Erasmus student exchange programme. This work was supported in part (A. L. S.) by The Netherlands Foundation of Chemical Research (SON) with financial aid from The Netherlands Foundation for Scientific Research (NWO).

Received, 9th August 1993; Com 3/04779B

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