Synthesis and Characterization of a Trigonal Monopyramidal Nickel(II) Complex

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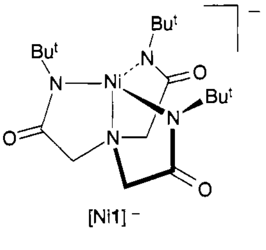
An unusual trigonal monopyramidal nickel(II) complex of a new tripodal tris-(*N-tert*-butylcarbamoylmethyl)aminato (3−) ligand is reported; this ligand sterically protects the Ni^{II} centre preventing further ligand coordination.

Trigonal monopyramidal (TMP) coordination geometry about a metal ion is rare. In synthetic systems, TMP complexes have been isolated using multidentate ligands whose geometric properties force the metal ion to adopt this unusual ligand arrangement. Notable examples include the tris(alkylsilylamido)amine ligands used by Verkade[1] and Schrock[2] and the tris(diphenylphosphinoethyl)amine ligands of Sacconi and Mealli.[3,4] These ligands share an important structural feature: sterically bulky R (R = alkyl, aryl) groups appended from equatorially bound donor atoms limit the access of exogenous ligands to the coordinatively unsaturated metal centre. However, in these ligands, the shielding provided by the bulky R groups is incomplete, as shown by the additional isolation of several trigonal bipyramidal metal complexes with these ligands.[2b,4,5] In order to examine a more constrained TMP coordination sphere, we have developed the tripodal ligand $[\mathbf{1}]^{3-}$ $\{H_3\mathbf{1} = N[CH_2C(O)NHBu^t]_3\}$, which contains a tertiary amine and three deprotonated amides with appended Bu^t groups.[6] We report here the synthesis, structure and electrochemical properties of the Ni^{II} complex of $[\mathbf{1}]^{3-}$. Preliminary studies suggest that $[\mathbf{1}]^{3-}$ prevents the binding of additional ligands and thus strictly enforces a TMP coordination geometry around the Ni^{II} centre.

The Ni^{II} complex was synthesized by the following procedure: $H_3\mathbf{1}$ (0.444 g, 1.24 mmol) was dissolved in dry DMF (10 ml) under an Ar atmosphere and treated with solid KH (0.152 g, 3.8 mmol). When gas evolution ceased $[Ni(Me_2SO)_6](ClO_4)_2$[7] (0.904 g, 1.24 mmol) was added to the mixture in one portion. After stirring (1 h), the solution was concentrated to 3 ml, filtered, washed with MeCN and diethyl ether, and dried under vacuum. The resulting orange solid was dissolved in DMF and Et_4NCl (0.21 g, 1.2 mmol) was added. This mixture was allowed to stir for 3 h after which volatiles were removed under vacuum. The orange $[Et_4N][Ni\mathbf{1}]$ was dissolved in THF (10 ml) and the potassium salts were removed by filtration. Orange crystals were obtained by diffusing diethyl ether into a THF solution of $[Et_4N][Ni\mathbf{1}]$ (57% overall yield from ligand).†

The molecular structure of $[Ni\mathbf{1}]^-$ is presented in Fig. 1.‡ This complex has a trigonal monopyramidal structure about the nickel(II) ion with the three amidate nitrogen donors of $[\mathbf{1}]^{3-}$ ligand coordinated equatorially. The Ni^{II} ion lies nearly in the trigonal plane formed by N(1)–N(3)–N(4); it is displaced by 0.14 Å toward the vacant coordination site. The apical N(2) is positioned perpendicular to the trigonal plane, resulting in an average N(2)–Ni–N_{amid} angle of 85.9(2)°. $[Ni\mathbf{1}]^-$ has nearly C_3 symmetry where the axis coincides with the Ni–N(2) bond. The average Ni^{II}–N_{amid} distance is 1.972(5) Å which is slightly shorter than the Ni–N(2) bond length [2.003(5) Å]. The Ni^{II}–N_{amid} and Ni^{II}–N_{am} distances observed in $[Ni\mathbf{1}]^-$ are similar to those found for various five- or six-coordinate, high-spin Ni^{II} complexes.[8]



$[Ni\mathbf{1}]^-$

The trigonal monopyramidal structure of $[Ni\mathbf{1}]^-$ is uncommon for four-coordinate Ni^{II} complexes for which square planar coordination geometry dominates.[9] We are aware of only one other synthetic Ni^{II} complex that appoaches a trigonal monopyramidal geometry, a Ni^{II} catenate reported recently by Sauvage and coworkers.[10] Comparison of the two structures shows that the Ni^{II} centre in the catenate has a structure slightly more distorted (toward tetrahedral) than that found in $[Ni\mathbf{1}]^-$: the Ni^{II} in the catenate is displaced 0.33 Å from the trigonal plane, in the direction of the apically coordinated donor.

Orange $[Ni\mathbf{1}]^-$ does not appear to form trigonal bipyramidal complexes *via* coordination of an exogeneous ligand. Dissolving $[Ni\mathbf{1}]^-$ in neat DMF or MeCN does not change the colour of the complex from that observed in THF.† Pyridine, H_2O, Cl^- and NCS^- also do not exhibit any affinity for the Ni^{II} centre.† This lack of reactivity can be explained by the nearly complete shielding of the vacant coordination site in $[Ni\mathbf{1}]^-$ by the amide Bu^t groups. The molecular structure of $[Ni\mathbf{1}]^-$ shows that the Bu^t groups form a cavity that encompasses the Ni^{II} centre (Fig. 2). Each Bu^t group is oriented such that two methyl groups are positioned outside the cavity (C_{out} and $C_{out'}$) and arranged symmetrically about the amide carbonyl group [average angle between planes formed by O–C_{amid}–$N_{amid} : N_{amid}$–C_{Bu^t}–$C_{out(out')}$ is 55.4°]. This disposition causes the remaining methyl group (C_{in}) on each Bu^t to be positioned inside the cavity: the average Ni–N_{amid}–C_{Bu^t}–C_{in} dihedral angle is 9.4°. These C_{in} methyl groups block the entry of any incoming ligand into the cavity, preventing binding to the Ni^{II} centre.[11] This orientation of Bu^t methyl groups is likely the most favoured in solution, since rotation about the N_{amid}–C_{Bu^t} bonds will be hindered by the amide carbonyl groups.

At room temperature $[Ni\mathbf{1}]^-$ is high spin with $\mu_{eff} = 3.49\ \mu_B$, a value which is comparable to those found for other $S = 1$ Ni^{II} complexes.[12] The high-spin character of $[Ni\mathbf{1}]^-$ is not surprising—an extended Hückel calculation indicates that the d_{z^2} (a)

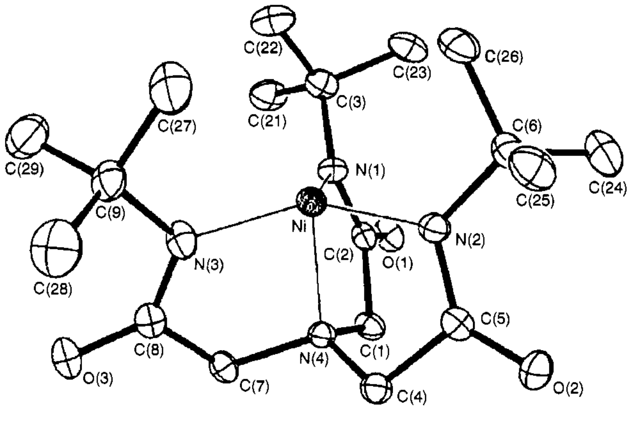


Fig. 1 ORTEP drawing of $[Ni\mathbf{1}]^-$ showing 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N(1) 1.975(5), Ni–N(2) 1.981(5), Ni–N(3) 1.960(5), Ni–N(4) 2.003(5), N(1)–Ni–N(2) 114.3(2), N(1)–Ni–N(3) 125.0(2), N(2)–Ni–N(3) 119.2(2), N(1)–Ni–N(4) 86.2(2), N(2)–Ni–N(4) 85.6(2), N(3)–Ni–N(4) 85.8(2).

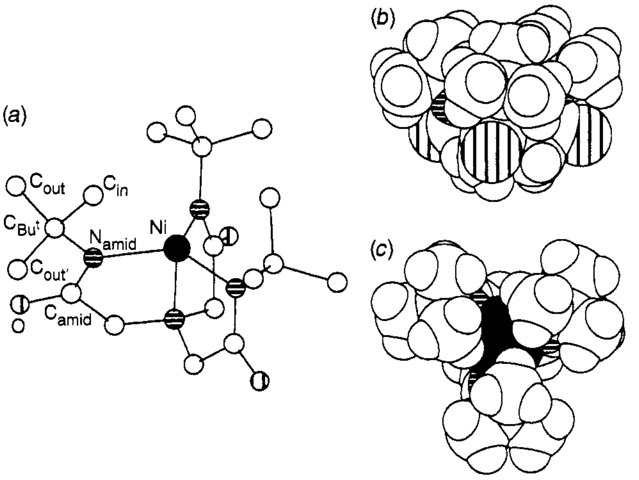


Fig. 2 View of the molecular structure of [Ni**1**]$^-$ illustrating (*a*) the arrangement of the Bu^t groups, spacing-filling representations of [Ni**1**]$^-$ showing (*b*) the orientation of the amide Bu^t groups, and (*c*) the steric protection provided to the Ni^{II} centre

orbital and the d_{xy}, $d_{x^2-y^2}$ (e) set of orbitals have similar energies and lie significantly higher than the d_{xz}, d_{yz} (e) set. CV shows that at a scan speed of 0.100 v s^{-1}, [Ni**1**]$^-$ has a quasi-reversible one-electron redox process at 0.56 V *vs.* SCE (ΔE_p = 0.073 V, $i_{pc}i_{pa}^{-1}$ = 0.80).§ Yet at slower scan speeds (*e.g.* v = 0.010 V s^{-1}) this redox process is irreversible. Attempts to chemically or electrochemically generate the oxidized product(s) at room temperature were unsuccessful: oxidation produces a transient violet species which changes rapidly to an EPR-silent brown material whose identity has yet to be determined. The violet-coloured species can be formed and stabilized (>48 h) at −75 °C by treating [Ni**1**]$^-$ with either $[Fe(bpy)_3]^{3+}$ or Ce^{IV} in a 2:1 mixture of propionitrile–DMF. The EPR spectrum of the oxidized solution measured at 77 K has considerable g-tensor anisotropy and g_{av} = 2.16 which are indicative of a metal-centred oxidation.[13] We tentatively assign this EPR spectrum to a Ni^{III} complex in an $S = \frac{1}{2}$ spin state[14] yet the identity and structure of this species is currently unknown. The rhombic character of the spectrum does suggest that this oxidized complex is distorted from a trigonal monopyramidal structure (which we expect would give a more axial specturm). Distortions in the *xy*-plane arising from Jahn–Teller effects could account for this apparent structural change.¶ Studies aimed at determining the structure of this high valent species and those of other metal complexes containing [**1**]$^{3-}$ are in progress.

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Footnotes

† *Selected data* for [Et$_4$N)(Ni**1**]: FTIR (Nujol) νcm^{-1} 3420b (H_2O), 1594s (CO, amide); magnetic moment μ_{eff} = 3.49 μ_B (solid), μ_{eff} = 3.49 μ_B (MeCN);[15] λ_{max}/nm (THF) 292 (ε/dm^3 mol^{-1} cm^{-1} 3240), 331 (4430), 473 (57), 512 (58), 876 (22); (MeCN) 288 (2930), 327 (3780), 473 (49), 511 (51), 877 (20); (DMF) 475 (53), 511, (52), 874 (20); (MeCN + py) 471 (50), 511 (52), 875 (21); (MeCN + Cl^-) 473 (51), 512 (53), 878 (20); (DMF + NCS^-) 473 (51), 511 (52), 878 (20).

‡ *Crystal data* for [Et$_4$N][Ni**1**]·C_4H_8O: space group $P2_1/c$, a = 13.162(3), b = 11.279(2), c = 25.566(6) Å, β = 104.09(3)°, V = 3681.2(14) Å^3, Z = 4. Of 4949 reflections collected (Mo-Kα, 4° ≤ 2θ ≤ 45°, 238 K) 4820 were independent and 2564 [F > 4.0σ(F)] were observed. The structure was solved by direct methods and refined anisotropically to R = 0.0646 and R_w = 0.0990 with a GOF = 1.21. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Ferrocinium/ferrocene couple was used as the internal standard: (ΔE_p = 0.070 V, $i_{pc}i_{pa}^{-1}$ *ca.* 1.0). No reductive processes were observed for [Ni**1**]$^-$ to −2.0 V *vs.* SCE in acetonitrile.

¶ EPR (EtCN–DMF, 77 K): g_1 = 2.29, g_2 = 2.16, g_3 = 2.03, a_3 = 20 G; when generated at −40 °C in 1 : 1 MeCN : DMF a slightly different rhombic EPR spectrum is obtained: G_1 = 2.22, g_2 = 2.16 and g_3 = 2.03, a_3 = 20 G. A small peak at g = 2.29 is also present.

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