Pentanuclear Complex Formed between Dinuclear Nickel(II) Complexes and Sodium Ion

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A new pentanuclear complex containing four nickel(II) ions and a sodium ion, \([\text{Na}[\text{Ni}_2(\text{O}_2\text{CMe})_2(\mu-\text{O}_2\text{CMe})]_2]\text{BPh}_4\) (I), was prepared using a binucleating ligand, \(N,N'\text{-bis}[2-(N,N'\text{-dimethyl})\text{aminoethyl}]-N,N'\text{-dimethyl}-1,3\text{-diamino}-2\)-hydroxypropane (HL). The crystal structure of I was determined by single-crystal X-ray crystallography. The compound crystallized in the triclinic space group \(P\overline{1}\) and \(Z = 2\) with cell parameters \(a = 10.841(3)\AA, b = 19.161(5)\AA, c = 20.415(5)\AA, \alpha = 116.929(18)^\circ, \beta = 92.970(19)^\circ, \gamma = 101.485(13)^\circ, V = 3655.7(19)\AA^3\). The \(R\) and \(wR\) (all data) values were 0.0464 and 0.1207, respectively, for 16641 independent reflections. Four of the oxygen donors in the coordinated bidentate acetato ligands further coordinated to one sodium ion in a tetrahedral manner.

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Binucleating ligands, which have two chelating side arms linked by various functional groups to attract two metal ions, have been widely used in the design of active-site models with two metal ions.1–3 A number of dinickel(II) complexes with binucleating ligands have been synthesized as models for the active site of urease.3,4 The results of these synthetic studies revealed that two dinickel(II) complexes with some binucleating ligands aggregated into dimeric species in the solid state by further coordination of bridging ligands. Although reports of these tetranuclear nickel(II) complexes are common,3,5,6 heteropolynuclear nickel(II) complexes containing other metal ions are very rare. The present study describes the synthesis of a new pentanuclear complex composed of four nickel(II) ions and a sodium ion, \([\text{Na}[\text{Ni}_2(\text{O}_2\text{CMe})_2(\mu-\text{O}_2\text{CMe})]_2]\text{BPh}_4\) (I) (Fig. 1), using a binucleating ligand, HL, and acetato ligands. The structure of the complex was determined using single-crystal X-ray crystallography.

The binucleating ligand, HL, was prepared according to a previously reported method.7 Complex I was prepared by refluxing an ethanol solution (20 mL) containing HL (0.10 g, 0.038 mmol) and nickel(II) acetate tetrahydrate (0.19 g, 0.076 mmol) for 30 min, followed by the addition of NaBPh4 (0.065 g, 0.019 mmol). The mixture was heated under reflux for an additional 1 h to give a clear green solution, which was evaporated to dryness (it is necessary to remove the solvent as much as possible). The resulting residue was recrystallized from nitromethane/diethyl ether by vapor diffusion to afford green crystals suitable for single-crystal X-ray analysis (yield of I: 0.17 g, 62%). Anal. Found: C, 51.40; H, 6.71; N, 8.00%. Calcd. for C62H100BN8NaNi4O14: C, 51.35; H, 6.95; N, 7.73%.

Table 1 Crystal and experimental data

| Chemical formula: C62H100BN8NaNi4O14 | Formula weight = 1450.12 |
|-------------------------------------|--------------------------|
| Crystal system: triclinic           | Space group: \(P\overline{1}\) |
| \(a = 10.841(3)\AA\)                | \(\alpha = 116.929(18)^\circ\) |
| \(b = 19.161(5)\AA\)               | \(\beta = 92.970(19)^\circ\) |
| \(c = 20.415(5)\AA\)               | \(\gamma = 101.485(13)^\circ\) |
| \(V = 3655.7(19)\AA^3\)           | \(Z = 2\) |
| No. of reflections collected = 37548 | |
| No. of independent reflections = 16648 | |
| \(\theta\) range for data collection: 1.13 to 27.516\(^\circ\) | |
| Data/Restraints/Parameters = 16641/0/829 | |
| Goodness-of-fit on \(F^2\) = 1.070  | |
| \(R\) indices: \(I > 2\sigma(I)\): \(R_1 = 0.0464, wR_2 = 0.1016\) | |
| \(R\) indices (all data): \(R_1 = 0.0689, wR_2 = 0.1207\) | |
| \((\Delta \rho)_{\text{max}} = 0.65\) eÅ\(^{-3}\) | \((\Delta \rho)_{\text{min}} = -0.53\) eÅ\(^{-3}\) |
| Measurement: Rigaku XtaLAB mini Program system: CrystalClear, CrystalStructure 4.2, SHEXL2014/7 |
| Structure determination: SIR2014 CCDC deposition number: 1821821 |

Fig. 1 Chemical structure of \([\text{Na}[\text{Ni}_2(\text{O}_2\text{CMe})_2(\mu-\text{O}_2\text{CMe})]_2]\text{BPh}_4\) (I).

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IR (KBr): $\nu$(COO–): 1601, 1570 cm$^{-1}$. VIS (diffuse reflectance): $\lambda_{\text{max}}$: 397, 656 nm.

Crystal and experimental data are listed in Table 1. The structure was solved using the direct method (SIR2014) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on $F^2$ was based on 16641 observed reflections and 829 variable parameters, and satisfactory converged with $R_1 = 0.0464$ [$I > 2\sigma(I)$].

The structure for 1 is shown in Fig. 2. Selected bond distances and angles are listed in Table 2. Two units of dinickel(II) complex (Ni1–Ni2: 3.535(1)Å, Ni3–Ni4: 3.536(1)Å) with L and acetato ligands that enclosed one sodium ion to form the hetero pentanuclear NaNi4 complex, 1, in which nickel(II) ions adopted distorted octahedral coordination geometries. Each nickel(II) ion was associated with two nitrogen donors and the $\mu$-alkoxide bridge of L, one bidentate acetato ligand, and a $\mu$-acetato bridge, while the sodium ion was surrounded by four oxygen donors in the coordinated bidentate acetato ligands. The average bond distances for Ni–N and Ni–O were 2.129 and 2.091 Å, respectively, which are typical values for high-spin octahedral nickel(II) complexes.  

The angle between two mean planes formed from O27–Na1–O32 and O67–Na1–O72 was 73$^\circ$, which suggests that the sodium ion is in a distorted tetrahedral coordination environment.

Thus, results revealed that dinickel(II) complexes with dinucleating ligand L and acetato ligands formed a dimeric structure suitable for capturing of a sodium ion, and forming a hetero pentanuclear NaNi4 complex.

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