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## A Nickel(II) Azide Cubane: Characterization of the Magnetic Exchange Interactions Mediated by a Triply Bridging Azide Group Bound End-On\*\*

Malcolm A. Halcrow, John C. Huffman, and George Christou\*

We have a long-standing interest in manganese carboxylate aggregates as models for the  $Mn_4$  cluster in the active center of green plants and cyanobacteria for photosynthetic water oxidation.<sup>[1]</sup> We prepared several  $Mn^{III}_3Mn^{IV}$  complexes containing the distorted cubane  $[Mn_4O_3X]^6+$  core ( $X$  = halide, carboxylate),<sup>[2]</sup> and also the cubane  $[Co_4O_4]^{4+}$  core, together with protonated versions of the latter.<sup>[3]</sup> As an extension to this work, we

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recently turned our attention to cubane complexes containing other metal ions, to investigate the electronic and magnetic properties of this interesting class of compound further. We report here the cubane complex **1**; this is the first paramagnetic



molecule to contain end-on-coordinated, triply bridging azide ligands,<sup>[4–6]</sup> and thus provides an opportunity to characterize the magnetic exchange interactions mediated by azide in this rare bridging mode. The structure of one other  $[M_4(N_3)_4]^{n+}$  cubane species is known, namely diamagnetic  $[Pt_4(N_3)_4(CH_3)_12]$ .<sup>[5]</sup>

A one-pot reaction of  $Ni(ClO_4)_2 \cdot 6H_2O$ ,  $NaN_3$ , and  $Na(dbm)$  (in a 1:1:1 molar ratio) in EtOH at room temperature yields a bright green precipitate containing **1** and a little  $NaClO_4$ . Recrystallization from  $CH_2Cl_2/EtOH$  affords large green crystals of pure **1** in 78% overall yield. The IR spectrum of **1** as a Nujol mull shows, in addition to bands arising from  $dbm^-$  and coordinated EtOH, a very strong absorption at  $2087\text{ cm}^{-1}$  attributable to the  $v_{\text{asym}}$ (N-N-N) stretching vibration of coordinated azide;<sup>[7]</sup> this band appears at  $2089\text{ cm}^{-1}$  in  $CHCl_3$  solution. The  $v_{\text{sym}}$ (N-N-N) and  $\delta$ (N-N-N) vibrations also expected from a metal-bound azide<sup>[7]</sup> were masked by absorptions from the  $dbm^-$  ligand and could not be positively identified. The UV/Vis spectrum of **1** in  $CHCl_3$  is typical of an octahedral  $Ni^{II}$  complex,<sup>[8]</sup> while the  $^1H$  NMR spectrum of **1** in  $CDCl_3$  shows the paramagnetically shifted resonances of only a single environment for  $dbm^-$  and EtOH.

The structure of the bis(toluene) solvate of **1** (Fig. 1)<sup>[9]</sup> contains a tetrานuclear  $[Ni_4(\mu_3-N_3)_4]^{4+}$  cubane core; the molecule has virtual  $C_2$  symmetry and lies on a general position within the unit cell. Each Ni ion is octahedrally coordinated by three end-on-coordinated, triply bridging azide ligands, one chelating  $dbm^-$  ligand, and one ethanol ligand. Each ethanol ligand is intramolecularly hydrogen-bonded to an O atom in a  $dbm^-$  ligand that is

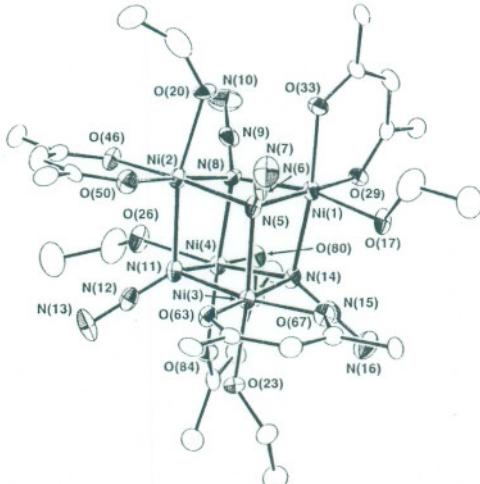


Fig. 1. ORTEP representation of complex **1** (ellipsoids at the 50% probability level). For clarity, only the *ipso* carbon atoms of the  $dbm^-$  phenyl rings are shown. Selected distances [Å] and angles [ $^\circ$ ]:  $Ni(1) \cdots Ni(2)$  3.168(1),  $Ni(1) \cdots Ni(3)$  3.146(1),  $Ni(1) \cdots Ni(4)$  3.231(1),  $Ni(2) \cdots Ni(3)$  3.239(1),  $Ni(2) \cdots Ni(4)$  3.177(1),  $Ni(3) \cdots Ni(4)$  3.156(1),  $Ni(1) \cdots Ni(5)$  2.141(5),  $Ni(1) \cdots Ni(8)$  2.136(6),  $Ni(1) \cdots Ni(14)$  2.094(5),  $Ni(2) \cdots Ni(5)$  2.117(5),  $Ni(2) \cdots Ni(8)$  2.111(5),  $Ni(2) \cdots Ni(11)$  2.138(6),  $Ni(3) \cdots Ni(5)$  2.132(6),  $Ni(3) \cdots Ni(11)$  2.100(5),  $Ni(3) \cdots Ni(14)$  2.132(5),  $Ni(4) \cdots Ni(8)$  2.109(6),  $Ni(4) \cdots Ni(11)$  2.150(5),  $Ni(4) \cdots Ni(14)$  2.113(6),  $Ni(1) \cdots Ni(5) \cdots Ni(2)$  96.1(2),  $Ni(1) \cdots Ni(5) \cdots Ni(3)$  94.8(2),  $Ni(2) \cdots Ni(5) \cdots Ni(3)$  99.4(2),  $Ni(1) \cdots Ni(8) \cdots Ni(2)$  96.5(2),  $Ni(1) \cdots Ni(8) \cdots Ni(4)$  99.1(2),  $Ni(2) \cdots Ni(8) \cdots Ni(4)$  97.7(2),  $Ni(2) \cdots Ni(11) \cdots Ni(3)$  99.7(2),  $Ni(2) \cdots Ni(11) \cdots Ni(4)$  95.6(2),  $Ni(3) \cdots Ni(11) \cdots Ni(4)$  95.9(2),  $Ni(1) \cdots Ni(14) \cdots Ni(3)$  96.2(2),  $Ni(1) \cdots Ni(14) \cdots Ni(4)$  100.4(2),  $Ni(3) \cdots Ni(14) \cdots Ni(4)$  96.1(2).

bound to a neighboring Ni atom (averaged  $O \cdots O = 2.703 \text{ \AA}$ ); this results in a distortion of the  $[Ni_4(N_3)_4]^{4+}$  core from  $T_d$  to  $D_{2d}$  symmetry which results in the four faces of the cubane spanned by hydrogen bonds having shorter Ni–Ni distances and more acute Ni–N–Ni angles and Ni–N–Ni dihedral angles than the two faces not bridged in this fashion (average values for  $Ni1-N5-N8-Ni2$ ,  $Ni1-N5-N14-Ni3$ ,  $Ni2-N8-N11-Ni4$ , and  $Ni3-N11-N14-Ni4$ :  $Ni \cdots Ni = 3.162 \text{ \AA}$ ,  $Ni-N-Ni = 96.1^\circ$ ,  $Ni-N-Ni = 167.1^\circ$ ; for  $Ni1-N8-N14-Ni4$  and  $Ni2-N5-N11-Ni3$ :  $Ni \cdots Ni = 3.235 \text{ \AA}$ ,  $Ni-N-Ni = 99.6^\circ$ ,  $Ni-N-Ni = 175.5^\circ$ ). This feature is also exhibited by several  $[Ni_4(OR)_4]^{4+}$  cubanes that contain coordinated alcohol ligands intramolecularly hydrogen bonded in this manner.<sup>[10, 11]</sup> The azide ligands are each symmetrically coordinated to three Ni ions, and the Ni–N distances and Ni–N–N angles about each azide show only small differences with no discernable pattern. The Ni–N and Ni–O bond lengths for **I** are unremarkable, while the N–N distances within the azide ligands display the same “long–short” pattern shown by  $Ni^{II}$  complexes containing end-on-coordinated, doubly bridging azides.

Variable-temperature magnetic susceptibility measurements were performed on a powder sample of **I** between 320 and 5.00 K. The observed effective magnetic moment  $\mu_{\text{eff}}$  for **I** rises from a value of  $6.46 \mu_B$  at 320 K to a maximum of  $9.66 \mu_B$  at 20 K, before slightly decreasing below 20 K (Fig. 2); the value at 20 K may

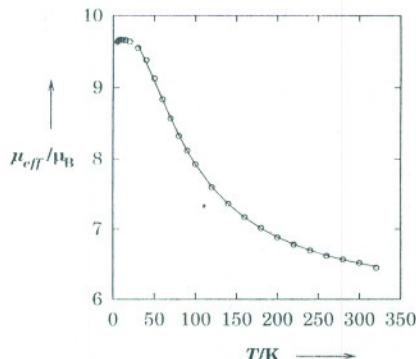


Fig. 2. A plot of effective magnetic moment  $\mu_{\text{eff}}$  per  $Ni_4$  unit vs. temperature  $T$  for complex **I**. The solid line represents the least-squares fit to a one- $J$  ( $T_d$  symmetry) model; see the text for the fitting parameters. Only data for  $T \geq 30 were employed to avoid problems at lower temperature arising from zero-field splitting of the  $S = 4$  ground state.$

be compared with the spin-only ( $g = 2$ ) value of  $8.94 \mu_B$  calculated for an  $S = 4$  ground state expected for four ferromagnetically coupled high-spin  $Ni^{II}$  ions. The data for temperatures  $\geq 30 were fit according to a one- $J$  model ( $T_d$  symmetry) incorporating a Weiss constant  $\theta$  to account for intermolecular interactions in the solid state<sup>[11]</sup> (fitting parameters  $J = +11.9 \pm 0.5 \text{ cm}^{-1}$ ,  $g = 2.05$ ,  $\theta = +3.0 \text{ K}$ ;  $\mathcal{H} = -2JS_1 \cdot S_2$ ; Fig. 2); utilization of a two- $J$  model ( $D_{2d}$  symmetry) did not result in improved fits or in significant splitting ( $<0.1 \text{ cm}^{-1}$ ) of the two  $J$  parameters.$

It is interesting that the distortions within the cubane core noted above are not reflected in the magnetic properties of **I**; this contrasts with the behavior of alkoxide-bridged cubanes, which show  $J$  values that are very sensitive to the Ni–O–Ni bridging angles within the faces of the cubane structure.<sup>[11–13]</sup> Specifically, the complex  $[Ni_4(OMe)_4(dbm)_4(MeOH)_4]$ , which exhibits similar patterns of MeOH  $\cdots dbm$  hydrogen bonding and structural distortions within the  $[Ni_4(\mu_3-OMe)_4]^{4+}$  unit, is best described by a two- $J$  model incorporating both ferromagnetic and antiferromagnetic contributions.<sup>[12]</sup> The observed  $J$

value for **I** is weaker than any reported for coupling across a  $[Ni_2(\eta^1,\mu-N_3)_2]$  bridge, consistent with the presence of triply, as opposed to doubly bridging azides in **I**.<sup>[14]</sup>

Two mechanisms for the transmission of superexchange interactions through azide ligands bridging end-on have been proposed, which involve accidental orthogonality<sup>[15]</sup> or spin polarization<sup>[16]</sup> as the dominant factor determining the sign of the observed coupling; both of these models predict ferromagnetic coupling between metal ions bridged by azide in end-on fashion in most (accidental orthogonality) or all (spin polarization) cases. In particular, a theoretical study of accidental orthogonality in  $Cu^{II}$  complexes containing a planar  $[Cu_2(\eta^1,\mu-N_3)_2]^{2+}$  bridge predicted a switch from ferromagnetic to antiferromagnetic coupling for Cu–N–Cu angles greater than  $103^\circ$ .<sup>[15]</sup> In this regard, it is noteworthy that the average Ni–N–Ni bridge angle in **I** is  $97.3^\circ$ , which is unusually small for an azide bridging end-on in a dinuclear metal complex and is substantially below the predicted crossover value. While the use of  $Ni^{II}$  rather than  $Cu^{II}$  as metal center and the nonplanarity of the  $[Ni_2(\mu-N_3)_2]$  bridges in **I** might be expected to cause small deviations from the published model,<sup>[17]</sup> the nature of the magnetic interactions present should be similar in the two types of compound, since both  $Ni^{II}$  and  $Cu^{II}$  only possess magnetic orbitals of  $\sigma$  symmetry. The lack of dependence of the coupling constant  $J$  on the Ni–N–Ni angle in **I** is difficult to reconcile on the basis of the accidental orthogonality model, but is consistent with the spin polarization model.<sup>[16]</sup> However, antiferromagnetic coupling mediated by end-on-coordinated, doubly bridging azide groups with an even more acute Ni–N–Ni angle of  $84^\circ$  was reported.<sup>[18]</sup> Clearly, the mechanism of superexchange coupling through end-on azide bridging ligands deserves further study, and the present work has provided an additional bridging mode for inclusion in these considerations.

### Experimental Procedure

Solid  $NaN_3$  (0.30 g, 4.9 mmol) and Na(dbm) (1.2 g, 4.9 mmol) were added to a solution of  $Ni(ClO_4)_2 \cdot 6H_2O$  (1.8 g, 4.9 mmol) in EtOH (100 mL), and the mixture was stirred at room temperature for 4 h. The resultant green precipitate was filtered off, washed with EtOH, and dried in air. Recrystallization from  $CH_2Cl_2/EtOH$  afforded deep green blocks, which were not of X-ray quality (1.4 g, 78%); crystallization from toluene/EtOH gave a lower yield of crystals suitable for an X-ray diffraction study. Correct C,H,N,Ni analysis for  $C_{68}H_{68}N_{12}O_{12}Ni_4$ . IR (Nujol):  $\tilde{\nu} = 3586$  (w), 3270 (br), 3061 (w), 2087 (vs), 1618 (w), 1595 (s), 1554 (s), 1516 (s), 1454 (m), 1442 (w), 1402 (m), 1383 (s), 1312 (s), 1292 (m), 1267 (w), 1242 (m), 1229 (w), 1183 (w), 1157 (w), 1129 (w), 1086 (w), 1073 (w), 1057 (m), 1047 (m), 1024 (m), 1001 (w), 941 (m), 882 (w), 785 (w), 754 (m), 725 (s), 691 (m), 637 (m), 530 (m)  $\text{cm}^{-1}$ . IR ( $CHCl_3$ ):  $\tilde{\nu} = 2089 \text{ cm}^{-1}$ . UV/Vis ( $CHCl_3$ ):  $\lambda_{\text{max}} (\epsilon_{\text{max}})$ : 246 (sh), 258 (85,520), 280 (sh), 364 (77,610), 412 (sh), 652 nm ( $41 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 57.2, 50.4$  ( $CH_3CH_2OH$ ), 12.8, 11.7, 10.2, 9.3 (dbm o-, m- and p-phenyl,  $CH_3CH_2OH$ ), -17.3 (dbm meso-CH).

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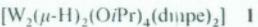
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[9] Crystal data for 1:  $C_{68}H_{68}N_{12}O_{12}Ni_4 \cdot 2C_7H_8$ , monoclinic,  $P2_1/n$ ,  $T = -174^\circ\text{C}$ ,  $a = 14.295(2)$ ,  $b = 23.203(4)$ ,  $c = 24.542(4)$  Å,  $\beta = 100.49(1)^\circ$ ,  $V = 8004.2$  Å $^3$ ,  $Z = 4$ ,  $6^\circ < 2\theta < 45^\circ$ , 991 refined parameters, 6163 unique reflections with  $F > 2.33\sigma(F)$ ;  $R = 0.0512$ ,  $R_w = 0.0444$ . Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, CB2-1EZ (UK), on quoting the full journal citation.  
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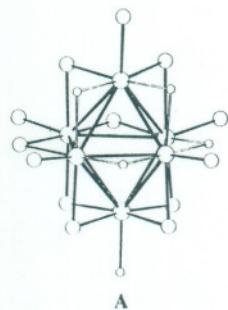
plex involving nonbridged W–W bonds between tungsten atoms in oxidation states +5 and 0.

The compound  $[W_2(iBu)_2(OiPr)_4]$  and dihydrogen react in hydrocarbon solvents to give the hexanuclear hydridotungsten cluster  $[W_6(H)_5(OiPr)_13]$ <sup>[12]</sup> whose  $W_6H_5O_{13}$  core is shown pictorially by A in Scheme 1. We reasoned that  $[W_6(H)_5(OiPr)_13]$  was formed stepwise from the coupling of reactive  $[W_2(H)_2(OiPr)_4]$  fragments. Ligand scrambling may account for the odd number of hydrido and alkoxido ligands in the product, and the formal oxidation state of each tungsten atom is maintained at +3.

Consequently in an attempt to trap  $[W_2(H)_2(OiPr)_4]$  we have carried out the hydrogenation of  $[W_2(iBu)_2(OiPr)_4]$  in the presence of chelating diphosphanes.<sup>[13]</sup> In the presence of bis(dimethylphosphano)ethane (dmpe), the dinuclear complex **I**



was obtained as a dark brown crystalline solid. The solid-state structure of **I** (Fig. 1) reveals that one W atom is coordinated to four OiPr ligands and the other to two dmpe ligands. The structure is superficially similar to that of  $[Mo_2(OiPr)_4(dmpe)_2]$ ,<sup>[14]</sup> but the M–M distance in **I** (M = metal) is notably longer and



Scheme 1. The  $W_6H_5O_{13}$  core A in  $[W_6(H)_5(OiPr)_13]$ .

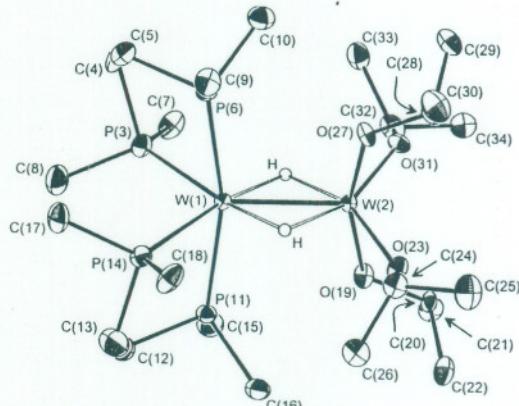


Fig. 1. ORTEP drawing showing the crystal structure of **I** (50% probability ellipsoids). Pertinent bond lengths [Å] and angles [°], averaged where appropriate: W-W 2.496(1), W-O 1.96(1), W-P(6,11) 2.424(2), W(1)-P(3,14) 2.486(2), W-W-P(6,11) 97.5(1), W-W-P(3,14) 130.3(1), W-W-O(23,31) 120.3(2), W-W-O(19,27) 99.4(2).

the coordination of the M(dmpe)<sub>2</sub> units is different. In  $[Mo_2(OiPr)_4(dmpe)_2]$  all the Mo-Mo-P bond angles range from 98.0(1) to 100.8(1)°, and the Mo–Mo bond length of 2.236(1) Å is typical for a Mo–Mo triple bond. In compound **I**, however, the W–W bond length of 2.496(1) Å is in the range expected for a W–W double bond, and two sets of W–W–P bond angles 97.5(1) and 130.3(1)° define four positions of the octahedral coordination about W(2). In the structure shown in Figure 1 the two  $\mu$ -H ligands are placed in proposed positions (hydride locating program XHYDEX),<sup>[15]</sup> and compound **I** is therefore formulated as  $[W_2(\mu-H)_2(OiPr)_4(dmpe)_2]$ . In solution compound **I** is fluxional; at low temperatures at least two isomers are present, as is evident from the hydride and phosphorus signals. Owing to the broadness of the <sup>31</sup>P NMR signals at –80 °C, the

## Complexes with Polar W–W Multiple Bonds: $[W_2(OiPr)_4L(dmpe)_2]$ ( $L = (H)_2$ , CO) and $[W_2(O)_4(\mu-O)\{W(CO)(dmpe)_2\}_2]^{**}$

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Dedicated to Professor F. A. Cotton  
on the occasion of his 65th birthday

The recent highlight by Herberhold and Jin<sup>[1]</sup> focused attention on heterometallic complexes with unbridged, polar metal–metal bonds. We describe here reactions in which a symmetric homonuclear complex containing a W–W triple bond yields asymmetric complexes with polar W–W bonds. One of the products described is a novel water-soluble tetranuclear com-

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