

**Syntheses, Magnetic Properties, and Crystal Structures of the Dimers [LNi( $\mu$ -N<sub>3</sub>)<sub>3</sub>NiL](ClO<sub>4</sub>) and [L'<sub>2</sub>Ni<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>( $\mu$ -N<sub>3</sub>)<sub>2</sub>] (L = *N,N',N'*-trimethyl-1,4,7-triazacyclononane; L' = 1,5,9-triazacyclododecane);  $\mu$ -Triazido- vs.  $\mu$ -Diazido-bridging**

Phalguni Chaudhuri,<sup>\*a</sup> Martina Guttman,<sup>a</sup> Dirk Ventur,<sup>a</sup> Karl Wieghardt,<sup>\*a</sup> Bernhard Nuber,<sup>b</sup> and Johannes Weiss<sup>b</sup>

<sup>a</sup> Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany

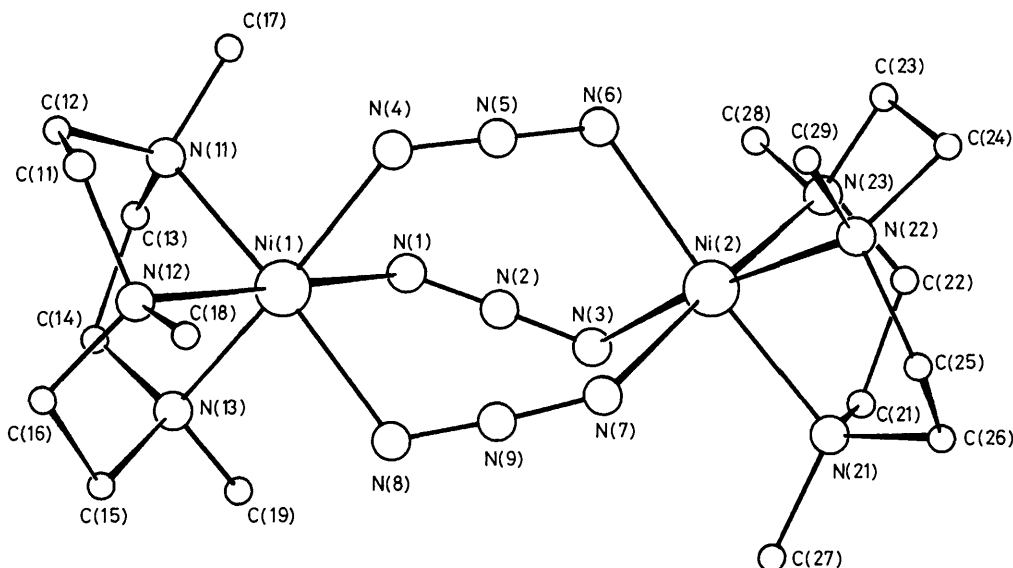
<sup>b</sup> Anorganisch-chemisches Institut der Universität, D-6900 Heidelberg, Federal Republic of Germany

The complexes [L<sub>2</sub>Ni<sub>2</sub>( $\mu$ -N<sub>3</sub>)<sub>3</sub>](ClO<sub>4</sub>) (**1**), [L<sub>2</sub>Ni<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>( $\mu$ -N<sub>3</sub>)<sub>2</sub>] (**2**), and [L'<sub>2</sub>Ni<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>( $\mu$ -N<sub>3</sub>)<sub>2</sub>] (**3**), where L and L' represent the cyclic triamines *N,N',N'*-trimethyl-1,4,7-triazacyclononane and 1,5,9-triazacyclododecane, have been synthesized and characterization of (**1**) and (**3**) by X-ray crystallography showed that (**1**) contains three end-to-end co-ordinated  $\mu$ -azido bridges, whereas (**3**) contains only two  $\mu$ -azido bridges and two monodentate N<sub>3</sub><sup>-</sup> ligands; the nickel centres in (**1**), (**2**), and (**3**) are strongly antiferromagnetically coupled.

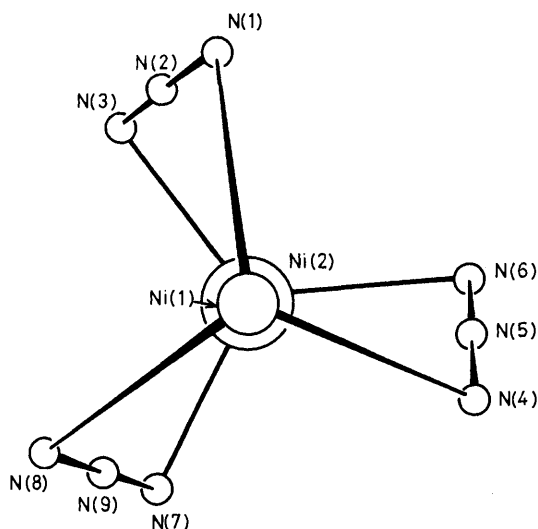
Intramolecular magnetic interactions in transition metal dimers have been studied extensively in the past in order to improve our understanding of the mechanisms of magnetic exchange on a structural basis using molecular orbital considerations.<sup>1</sup> Duggan and Hendrickson have studied magnetic exchange interactions in the following two nickel(II) dimers [Ni<sub>2</sub>(macro)<sub>2</sub>(N<sub>3</sub>)<sub>3</sub>]I and [Ni<sub>2</sub>(tren)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> where macro is 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane and tren is 2,2',2''-triaminoethylamine.<sup>2-4</sup> For the former an intradimer isotropic exchange parameter *J* of -12.3

cm<sup>-1</sup> and for the latter a value of -35.1 cm<sup>-1</sup> have been determined from variable-temperature magnetic susceptibility measurements.<sup>3,4</sup> Thus there is a weak and a moderately strong antiferromagnetic coupling of two nickel(II) centres in an octahedral environment (NiN<sub>6</sub>-donor set) propagated by one and two azido bridges, respectively.

We report here the synthesis, crystal structure, and magnetic properties of such a dimer containing *three*  $\mu$ -azido bridges. [LNi( $\mu$ -N<sub>3</sub>)<sub>3</sub>NiL](ClO<sub>4</sub>) (**1**) represents to the best of our knowledge the first example of a nickel(II) dimer with

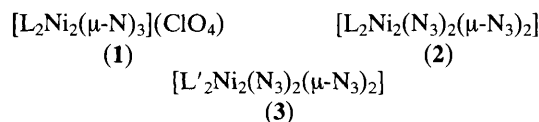


**Figure 1.** Structure of the dimeric monocation of (1). Selected bond distances (Å) and angles (°) of the  $\text{Ni}_2\text{N}_{15}$  core: Ni(1)–N(12) 2.096(8), Ni(1)–N(1) 2.166(9), Ni(1)–N(4) 2.110(10), Ni(1)–N(11) 2.105(9), Ni(1)–N(13) 2.072(9), Ni(1)–N(8) 2.170(10), Ni(2)–N(3) 2.119(11), Ni(2)–N(6) 2.160(10), Ni(2)–N(21) 2.095(9), Ni(2)–N(22) 2.093(10), Ni(2)–N(23) 2.119(9), Ni(2)–N(7) 2.142(9), N(4)–N(5) 1.162(14), N(8)–N(9) 1.164(15), N(5)–N(6) 1.185(15), N(7)–N(9) 1.193(15); Ni(1)–N(4)–N(5) 119.2(8), N(4)–N(5)–N(6) 177.7(8), N(5)–N(6)–Ni(2) 118.6(8), Ni(1)–N(1)–N(2) 116.4(7), N(1)–N(2)–N(3) 176.3(8), N(2)–N(3)–Ni(2) 120.1(8), Ni(1)–N(8)–N(9) 115.6(6), N(8)–N(9)–N(7) 178.2(6), N(9)–N(7)–Ni(2) 118.8(7), N(12)–Ni(1)–N(11) 84.3(5), N(4)–Ni(1)–N(1) 90.4(5), N(4)–Ni(1)–N(12) 92.1(5), N(12)–Ni(1)–N(13) 84.5(5), N(4)–Ni(1)–N(8) 89.7(5), N(4)–Ni(1)–N(11) 95.3(5), N(11)–Ni(1)–N(13) 83.4(5), N(1)–Ni(1)–N(8) 90.7(5), N(1)–Ni(1)–N(12) 174.7(8), N(1)–Ni(1)–N(13) 93.0(5), N(8)–Ni(1)–N(11) 174.6(8), N(8)–Ni(1)–N(13) 91.6(5).



**Figure 2.** Perspective view of the  $\text{Ni}_2(\mu\text{-N}_3)_3$  core of (1) down the Ni...Ni axis.

three end-to-end co-ordinated azide bridges.<sup>5</sup> A solution of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.2 g) in absolute methanol (40 ml) was refluxed with triethyl orthoformate for 30 min, after which time a solution of *N,N',N''*-trimethyl-1,4,7-triazacyclononane<sup>6</sup> (L) (0.7 g) in benzene (4 ml) was added, and the mixture refluxed for further 30 min. To the now deep green solution sodium azide (0.15 g), dissolved in methanol (10 ml), was added. Within a few minutes a greenish-white solid precipitated, which was filtered off and discarded. The clear green solution yielded *X*-ray quality green crystals of  $[\text{L}_2\text{Ni}_2(\mu\text{-N}_3)_3](\text{ClO}_4)$  (1), when left at room temperature (yield: 0.6 g).

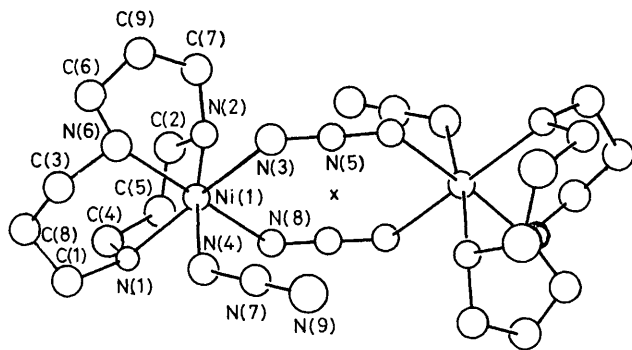


When the above preparation was carried out in the absence of perchlorate ions the green neutral complex  $[\text{L}_2\text{Ni}_2(\text{N}_3)_2(\mu\text{-N}_3)_2]$  (2) was obtained. Replacement of the cyclic ligand L by 1,5,9-triazacyclododecane (L') afforded the analogous neutral complex  $[\text{L}'_2\text{Ni}_2(\text{N}_3)_2(\mu\text{-N}_3)_2]$  (3). Complexes (2) and (3) were prepared by the following procedure.

To a solution of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.25 g) in absolute methanol (30 ml) was added a methanolic solution (1 M; 1.5 ml) of the respective amine L or L'. The solution was heated under reflux for 30 min and sodium azide (0.26 g) was added. This solution was refluxed for 10 min, after which time its volume was reduced by passing a stream of argon until bluish-green crystals of (2) or (3) precipitated (yield 40%).

The structure† of the binuclear cation of (1) is shown in Figure 1. The bridging azide groups are end-to-end coordinated and only slightly asymmetric. The two Ni–N–N angles of each ( $\mu\text{-N}_3$ )-bridge are nearly equal ( $\sim 119^\circ$ ); the

† *Crystal data* for (1) [and (3) in brackets]:  $M = 685.6$  [628.1], monoclinic [monoclinic], space group  $C2/c$  [ $P2_1/c$ ],  $a = 29.37(1)$  [8.112(3)],  $b = 15.031(6)$  [10.228(3)],  $c = 15.949(5)$  [16.060(5)] Å,  $\beta = 119.35(2)^\circ$  [91.66(3)°],  $Z = 8$  [2],  $D_m = 1.46$  [1.53],  $D_c = 1.483$  [1.56] g cm<sup>-3</sup>, crystal dimensions  $0.4 \times 0.15 \times 0.15$  [ $0.4 \times 0.1 \times 0.1$ ] mm<sup>3</sup>.  $R = 0.053$  [0.042] for 2223 [2781] reflections with  $I > 2.5 \sigma(I)$  collected at 20 °C on an AED II-Siemens [Syntex] diffractometer,  $\theta$ - $2\theta$  scan,  $2.5 < 2\theta < 55^\circ$  [60°], empirical absorption corrections have been carried out. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 3.** Structure of  $[L'_2Ni_2(\mu-N_3)_2(N_3)_2]$  (**3**) ( $\times$  denotes a centre of symmetry). Selected bond distances (Å) and angles ( $^\circ$ ) of the  $Ni_2N_{18}$  core: Ni–N(1) 2.101(3), Ni–N(2) 2.126(3), Ni–N(3) 2.135(3), Ni–N(4) 2.110(3), Ni–N(6) 2.101(3), Ni–N(8) 2.167(3), N(4)–N(7) 1.172(5), N(7)–N(9) 1.149(5), N(3)–N(5) 1.153(4), N(5)–N(8') 1.167(4); Ni–N(3)–N(5) 138.4(3), N(3)–N(5)–N(8') 175.9(3), N(3)–Ni–N(8) 92.4(1), N(4)–Ni–N(8) 88.6(1), N(3)–Ni–N(4) 88.3(1), N(2)–Ni–N(6) 92.2(1), N(1)–Ni–N(2) 96.5(1), N(1)–Ni–N(6) 93.2(1), Ni–N(4)–N(7) 124.4(3), Ni–N(8)–N(5') 124.4(2), N(4)–N(7)–N(9) 177.9(4), N(1)–Ni–N(4) 87.5(1), N(2)–Ni–N(3) 87.6(1), N(3)–Ni–N(6) 87.4(1).

Ni–N<sub>α</sub> and Ni–N<sub>γ</sub> distances are different (~2.16 vs. ~2.11 Å). Two of these shorter Ni–N bonds and one of the longer distances belong to Ni(2), whereas two longer and one shorter Ni–N bonds are associated with Ni(1). Therefore, the two nickel centres in the dimeric cation are inequivalent. Each nickel centre is co-ordinated facially to a cyclic amine L'. Figure 2 shows a projection of the  $Ni_2(\mu-N_3)_3$  core down the Ni...Ni axis indicating the dissymmetry of this core.

The halves of the dimeric molecule (**3**) are related by a crystallographic centre of symmetry (Figure 3). The Ni atom is in an octahedral environment of three facially co-ordinated nitrogen atoms, one nitrogen of a monodentate  $N_3^-$  ligand and two *cis*-nitrogen atoms of ( $\mu-N_3$ )-bridging groups. The eight-membered  $Ni_2(\mu-N_3)_2$  ring is approximately planar and the azido bridges are asymmetric with Ni–N–N bond angles of 138 and 124° and Ni–N distances of 2.135 and 2.167 Å. The geometry of the  $Ni_2(\mu-N_3)_2$  core is identical within experimental error with that of  $[Ni_2(tren)_2(\mu-N_3)_2](BPh_4)_2$ .<sup>4</sup> It is assumed that the structure of (**2**) is very similar.

It is noted that owing to the steric requirements of the ligands *N,N',N''*-trimethyl-1,4,7-triazacyclononane in (**1**) and (**2**), and of 2,2',2''-triaminotriethylamine in Hendrickson's complex,<sup>4</sup> the nickel centres are in a considerably distorted octahedral environment since the N–Ni–N bond angles of the amine nitrogens are smaller than 90°. This is not the case for (**3**). The twelve-membered macrocycle 1,5,9-triazacyclododecane allows N–Ni–N bond angles which are only slightly larger than 90° and, consequently, the  $NiN_6$  cores in (**3**) are nearly octahedral.

Variable-temperature magnetic susceptibility data (100–300 K; Faraday method) for (**1**)–(**3**) have been analysed using the simple isotropic Heisenberg dimer model<sup>7</sup> assuming a zero-field parameter  $D = 0$ . It has previously been noted that the value of the exchange parameter  $J$  for a nickel(II) dimer is

not influenced markedly by the value of either the zero-field splitting parameter  $D$  or the interdimer interaction  $Z'/J$ .<sup>8</sup> The  $Ni^{II}$  centres in (**1**)–(**3**) are strongly intramolecularly antiferromagnetically coupled.† The observed intradimer exchange constants are the largest observed to date in azido-bridged dimers of nickel(II).

In the dimeric complex  $[Ni_2(\text{macro})_2(N_3)_3]I$  with a *single* end-to-end azide bridge a relatively weak antiferromagnetic coupling is observed ( $J -12.3 \text{ cm}^{-1}$ ) which increases to  $-35$  and  $-47 \text{ cm}^{-1}$  in  $[Ni_2(\text{tren})_2(\mu-N_3)_2](BPh_4)_2$  and (**2**), respectively, complexes containing *two*  $\mu-N_3$ -bridges of similar symmetry.<sup>4</sup> In keeping with this trend an even stronger exchange coupling is observed for (**1**) which contains *three* end-to-end ( $\mu-N_3$ )-bridges.

Surprisingly, and rather unexpectedly, the strongest antiferromagnetic exchange coupling is observed for the doubly bridged (**3**) which is even stronger than in the triply bridged (**1**). The geometry of the  $Ni_2(\mu-N_3)_2$  core of (**3**) is the same as in  $[Ni_2(\text{tren})_2(\mu-N_3)_2](BPh_4)_2$  but the octahedral  $NiN_6$  cores of the latter complex are much more distorted than those in (**3**). This is a further example that changes of the non-bridging ligands can dramatically affect the magnitude of the antiferromagnetic interaction propagated by the same bridging ligands.<sup>9</sup>

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

Received, 28th June 1985; Com. 916

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† The calculated exchange coupling constants (and  $g$  values) are: (**1**):  $-71 \text{ cm}^{-1}$  (2.38); (**2**):  $-47.5$  (2.4); (**3**):  $-90$  (2.81). Electronic spectra were recorded in methanol containing sodium azide ( $10^{-2} \text{ mol dm}^{-3}$ ): (**1**): 593(26), 860(sh), and 960 nm ( $72 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ); (**2**): 591(20), 860(sh), 961(70); (**3**): 373(46), 615(44.5), and 996(34).