Binuclear Nickel Complexes with Single Azide Bridges. Structure and Properties of $[Ni_2(N,N\text{-bis(2-aminoethyl)-}N'\text{-(2-pyridylmethyl)ethane-1,2-diamine})_2(\mu\text{-}N_3)](ClO_4)_3$ and $[Ni_2(\text{1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane})_2(\mu\text{-}N_3)](ClO_4)_3$

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The mononuclear precursors $[Ni(trenpy)(OH_2)](ClO_4)_2$ (**1**) and $[Ni(dmptacn)(OH_2)](ClO_4)_2$ (**2**) have been used to prepare the corresponding azide bridged binuclear Ni(II) complexes $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$ (**3**), where trenpy is *N,N*-bis(2-aminoethyl)-*N'*-(2-pyridylmethyl)ethane-1,2-diamine, and $[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$ (**4**), where dmptacn is 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane. These complexes have been characterized using various physicochemical techniques. Single-crystal X-ray diffraction studies of $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$ have shown that the compound crystallizes in the monoclinic space group, *C*2/*c* (No. 15), with $a = 29.094(22)$ Å, $b = 8.292(6)$ Å, $c = 15.127(12)$ Å, $\beta = 92.93(6)°$, and Z = 4. Least-squares refinement gave final R and R_w values of 0.060 and 0.049, respectively, for 1401 observed reflections. The complex cation consists of two Ni(II) centers in distorted octahedral environment held together by a single azide bridge. The binuclear unit is centrosymmetric with a Ni–N(azide) bond distance of 2.133(7) Å, Ni–N–N angle of 131.6(5)°, and torsion angle of 0°. The Ni–N(amine) bond lengths (2.07–2.11 Å) are typical of Ni(II) amine complexes. The temperature dependence of the magnetic susceptibility for both complexes is typical of antiferromagnetically coupled binuclear Ni(II) complexes. Using the spin Hamiltonian, $-2J\hat{S}_1\cdot\hat{S}_2$, J values of -26.8 and -42.5 cm^{-1} were determined for **3** and **4**, respectively.

Introduction

The continuing interest in the structure and properties of binuclear metal complexes derives from their ability to model active sites present in some metalloproteins[1] and the search for a better understanding of the physicochemical properties of such complexes, in particular, the factors that affect magnetic interactions between paramagnetic centers.[2] Within this large range of binuclear complexes, doubly and triply bridged complexes are more common than complexes in which the metals are coupled through a single exogenous bridge. There are, however, well-known examples of transition metal complexes with, for example, single oxo,[3] hydroxo,[4] peroxo,[1d,5] imidazolato[6] and azido[7,8] bridges. The relative stability of doubly and triply bridged complexes over singly bridged complexes often means that when two or more adjacent sites are available multiple bridges are likely to form.

One approach to the synthesis of singly bridged complexes has involved the development of pentadentate ligands which block five coordination sites on an octahedral complex leaving only one site available for bridge formation. The ligands 4,7-bis(2-pyridylmethyl)-1-thia-4,7-diazacyclononane (dmptdacn, Chart 1)[9] and 4,7-bis(2-pyridylmethyl)-1-oxa-4,7-diazacyclononane (dmpodacn, Chart 1)[10] are two examples of such ligands whose coordination properties have been explored recently. We have previously investigated the coordination properties of the pentadentate ligand trenen (Chart 1)[11–13] and have reported the structure of $[(trenen)Co(O_2)Co(trenen)]^{4+}$.[11] This work has now been extended to the development of two new pentadentate ligands, *N,N*-bis(2-aminoethyl)-*N'*-(2-pyridylmethyl)ethane-1,2-diamine (trenpy, Chart 1) and 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (dmptacn, Chart 1) which are derivatives of tris(2-aminoethyl)amine (tren) and 1,4,7-triazacyclononane (tacn), respectively. The application of trenpy and dmptacn in the synthesis of binuclear nickel(II) complexes containing single azido bridges is reported here.

Escuer, Ribas, and co-workers[14–21] have carried out systematic investigations of azido-bridged nickel complexes which have

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(1) See, for example: (a) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1. (b) Kurtz, D.M., Jr., *Chem. Rev.* **1990**, *90*, 585. (c) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1980**, *38*, 99. (d) Kitajima, N.; Moro-oka, V. *J. Chem. Soc., Dalton Trans.* **1993**, 2665. (e) Solomon, E. J., Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521.

(2) See for example: Willet, R., Gatteschi, D., Kahn, O., Eds. *Magneto-Structrual Correlations in Exchange Coupled Systems*; NATO ASI Series C: Mathematical Sciences, Reidel: Dordrecht, The Netherlands, 1985; Vol. 40. Cairns, C. J.; Busch, D.H. *Coord. Chem. Rev.* **1986**, *69*, 1. McCarthy, P.; Güdel, H. *Coord. Chem. Rev.* **1988**, *88*, 69. Gorun, S. M.; Lippard, S. *Inorg. Chem.* **1991**, *30*, 1625.

(3) (a) West, B. O. *Polyhedron* **1989**, *8*, 219. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(4) Springborg, J. *Adv. Inorg. Chem.* **1988**, *32*, 55.

(5) (a) Miskowski, V. M. *Comments Inorg. Chem.* **1987**, *6*, 193. (b) Burgess, J.; Hill, H. A. O.; Tew, D. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D, McCleverty, J. A, Eds.; Pergamon: Oxford, England, 1987, Vol. 2, pp 295–333 and references therein.

(6) (a) Koch, C. A.; Reed, C. A.; Brewer, G. A.; Rath, N. P.; Scheidt, W. R.; Gupta, G.; Lang, G.; *J. Am. Chem. Soc.* **1989**, *111*, 7645. (b) Lu, Q.; Luo, Q. H.; Dai, A.B.; Zhou, Z. Y.; Hu, G. Z. *J. Chem. Soc., Chem. Commun.* **1990**, 1429. (c) Chaudhuri, P.; Karpenstein, I.; Winter, M.; Lengen, M.; Butzlatt, C.; Bill, E.; Trautwein, A. X.; Flürke, V.; Haupt, H.-J.; *Inorg. Chem.* **1993**, *32*, 888.

(7) Pierpont, C. G.; Hendrickson, D. N.; Duggan, D. M.; Wagner, F.; Barefield, E. K. *Inorg. Chem.* **1975**, *14*, 604.

(8) Bkouche-Walksman, I.; Boillot, M. L.; Kahn, O.; Sikorav, S. *Inorg. Chem.* **1984**, *23*, 4454.

(9) Wasielewski, K.; Mattes, R. *Acta Crystallogr.* **1990**, *C46*, 1826. Wasielewski, K.; Mattes, R. *Z. Anorg. Allg. Chem.* **1993**, *619*, 158.

(10) Szulbinski, W. S.; Warburton, P. R.; Busch, D. H.; Alcock, N. W. *Inorg. Chem.* **1993**, *32*, 297.

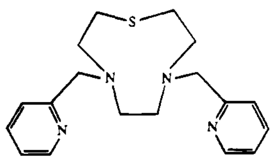
(11) Gatehouse, B. M.; McLachlan, G.; Martin, L. L.; Martin, R. L.; Spiccia, L. *Aust. J. Chem.* **1991**, *44*, 351.

(12) Giannos, M.; Fallon, G. D.; Spiccia, L. *Acta Crystallogr., Ser. C*, in press.

(13) Gatehouse, B. M.; Martin, R. L.; McLachlan, G.; Platts, S. N.; Spiccia, L. *Acta Crystallogr.* **1992**, *C48*, 271.

0020-1669/94/1333-4663$04.50/0

Chart 1



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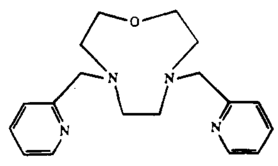

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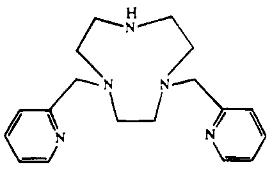

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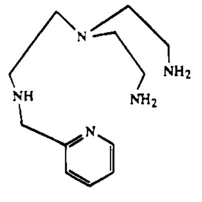
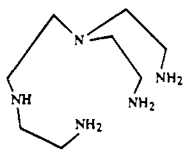


trenpy



trenen

established that the azide can coordinate in a variety of modes, end-to-end (μ-1,3), end-on (μ-1,1), and one example[16] where a single azide links three Ni(II) centers by adopting both end-to-end and end-on coordination modes. A variety of complexes have been prepared by these workers, which include binuclear complexes,[14,19,20] tetranuclear complexes,[17] and complexes which are one or two dimensional polynuclear networks.[15,16,18,21] Magnetic studies on these complexes have led to the conclusion that μ-1,3 coordination gives rise to antiferromagnetism (a magneto–structural correlation has been developed[20,21]) while μ-1,1 coordination induces ferromagnetism. So far, only one complex is known which contains a single azido bridge that is not part of a polymeric network. The complex, $[Ni_2(Me_4cyclam)_2(N_3)_2(\mu\text{-}1,3\text{-}N_3]^+$, where Me_4cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, shows weak antiferromagnetic coupling between the Ni(II) centers.[7] The synthesis and properties of two new complexes of this type, $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$ (**3**) and $[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$ (**4**), are presented in this paper.

Experimental Section

Materials and Reagents. All materials were of reagent grade unless indicated otherwise. Tacn·3HBr was prepared by a modification of the Richman-Atkins synthesis and has been described previously.[22]

Caution! *Although no problems were encountered in this work, perchlorate salts of transition metal complexes and azide metal complexes are potentially explosive. They should be handled with care and should only be prepared in small quantities.*

Preparation of 1,4-Bis(2-pyridylmethyl)-1,4,7-triazacyclononane (dmptacn). Tacn·3HCl (0.65 g, 2.44 mmol) and picolyl chloride hydrochloride (0.80 g, 4.88 mmol) were dissolved in water (20 mL). The pH of the solution was adjusted to 9 by the addition of 2 M NaOH. The resulting pale orange solution was stirred for 3 days by which time the pH had fallen to ca. 7. The pH of the solution was again adjusted to 9 and the solution was stirred for a further 3 days. The pH of the reaction mixture was then increased to ca. 13 and the free ligand was extracted into chloroform (6 × 70 mL) and the solution dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure yielding a yellow oil (yield: 0.36 g, 50%). The oil was converted into the less hygroscopic tetrahydrobromide by treatment with hydrobromic acid.

Characterization. Anal. Calcd for $C_{18}H_{25}N_5$·4HBr (hydrobromide salt): C, 33.8; H, 4.6; N, 11.0. Found: C, 34.0; H, 5.3; N, 11.0. NMR Spectra (free dmptacn): ^{13}C, 157.9, 148.9, 136.5, 122.6, and 122.2 ppm (pyridine ring carbons), 60.5 ppm ($pyCH_2$), 52.1, 48.8, and 44.9 ppm (tacn ring carbons); ^1H, 2.5–2.8 (m, 6H), 3.43 (bs, NH), 3.9 (s, 2H) $pyCH_2$, 7.11 (t, 1H) 7.48–7.65 (m, 2H), 8.5 (d, 1H). Mass spectrum (free dmptacn): m/z^+ 311.

Preparation of *N,N*-Bis(2-aminoethyl)-*N'*-(2-pyridylmethyl)-ethane-1,2-diamine (trenpy). A methanolic solution containing tris(2-aminoethyl)amine (1.46 g, 10 mmol) and pyridine-2-carboxaldehyde (1.07 g, 10 mmol) was stirred for 10 min, excess $NaBH_4$ (2 g, 52 mmol) was added, and the solution was stirred for 1 h. Dilute HCl was added to destroy the excess borohydride and the pH adjusted to 13 by the addition of 2 M NaOH. The free ligand was extracted into $CHCl_3$ (3 × 100 mL) and the solution dried over Na_2SO_4. After filtration the solution was taken to dryness under reduced pressure yielding a yellow oil (yield: 1.47 g, 62%).

Characterization. NMR spectra: ^{13}C, 159.4, 149.4, 136.7, 122.3, and 122.2 ppm (pyridine ring carbons), 64.3 ppm ($pyCH_2$), 56.7, 54.9, 47.0, and 39.8 ppm (CH_2 on tren), with minor peaks due to di- and trisubstituted tren also observed; ^1H, 2.4–3.4 ppm (broad multiplets, CH_2 on tren), 3.9 ppm ($pyCH_2$), and 7–8.5 ppm (complex multiplets, pyridine ring protons). Integration indicated some di-and trisubstituted products. Mass Spectrum: m/z^+ 328, 237.

$[Ni(trenpy)OH_2](ClO_4)_2 \cdot H_2O$ (1). An aqueous solution of trenpy was prepared by allowing pyridine-2-carboxaldehyde (0.169 g, 1.6 mmol in 25 mL of water) to react with tris(2-aminoethyl)amine (0.231g, 1.6 mmol in 25 mL of water). The resulting pale orange solution was stirred for 10 min, and $NaBH_4$ (0.3 g, 7.9 mmol) was added slowly and the solution stirred for another 60 min. After the excess borohydride was destroyed with acid, the pH of the solution was adjusted to 7 and $Ni(NO_3)_2 \cdot 6H_2O$ (0.46 g, 1.6 mmol) was added. The pink solution was diluted and adsorbed onto a cation exchange column (Dowex 50X-2). The compound was eluted with 1 M $NaClO_4$. A small amount of $[Ni(tren)(OH_2)_2]^{2+}$ eluted first followed by a major purple band. The purple eluent was concentrated to about half of the original volume and left to stand overnight. The purple microcystalline precipitate that had formed was collected by filtration and washed with ethanol (yield: 0.38 g, 45%).

Characterization. Anal. Calcd for $[Ni(C_{12}H_{23}N_5)OH_2](ClO_4)_2 \cdot H_2O$: C, 27.1; H, 5.1; N, 13.2. Found : C, 26.3; H, 5.0; N, 13.4. Electron microprobe: Ni:Cl ratio 1:2. Selected IR bands (cm^{-1}): 3448 (H_2O), 3300, 3167 (NH), 1609 (py), 1478 (py), 1445 (py), 1088, 624 (ClO_4^-). Molar conductivity (Λ_m in H_2O): 260 S cm^2 mol^{-1}.

$[Ni(dmptacn)OH_2](ClO_4)_2 \cdot H_2O$ (2). A solution of dmptacn (0.83 g, 2.66 mmol) in methanol (40 mL) was added to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.77 g, 2.66 mmol in 20 mL of methanol) and the solution stirred overnight. Sodium perchlorate (3 g) was then added, and the solution was cooled in an ice bath. The purple precipitate that formed was filtered and washed with ethanol and ether (yield: 1.43 g, 90%).

Characterization. Anal. Calcd for $[Ni(C_{18}H_{25}N_5)OH_2](ClO_4)_2 \cdot H_2O$: C, 35.7, H, 4.8; N, 11.6. Found: C, 35.7; H, 4.6; N, 11.5. Electron

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(14) Escuer, A.; Vicente, R.; Ribas, J. *J. Magn. Magn. Mater.* **1992**, *110*, 181.
(15) Vicente, R.; Escuer, A.; Ribas, J. *Inorg. Chem.* **1992**, *31*, 1726.
(16) Monfort, M.; Ribas, J.; Solans, X. *J. Chem. Soc., Chem. Commun.* **1993**, 350.
(17) Ribas, J.; Monfort, M.; Costa, R.; Solans, X. *Inorg. Chem.* **1993**, *32*, 695.
(18) Escuer, A.; Vicente, R.; Ribas, J.; El Fallah, M. S.; Solans, X. *Inorg. Chem.* **1993**, *32*, 1033.
(19) Vicente, R.; Escuer, A.; Ribas, J.; El Fallah, M. S.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1993**, *32*, 1920.
(20) Ribas, J.; Monfort, M.; Diaz, M.; Bastos, C.; Solans, X. *Inorg. Chem.* **1993**, *32*, 3557.
(21) Escuer, A.; Vicente, R.; Ribas, J.; El Fallah, M. S.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1993**, *32*, 3727.
(22) (a) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268. (b) Richman, J. E.; Oettle, W. F.; Atkins, T. J. *Org. Synth.* **1978**, *58*, 86. (c) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.

Table 1. Crystallographic Data for $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$[a]

chemical formula	$C_{24}H_{46}N_{13}Ni_2Cl_3O_{12}$	Z	4
fw	932.5	T, °C	−80(1)
space group	C2/c	λ, Å	0.71069
a, Å	29.094(22)	σ_{calc}, g cm^{-3}	1.70
b, Å	8.292(6)	σ_{meas}, g cm^{-3}	1.69(1)
b, Å	8.292(6)	μ(Mo Kα), mm^{-1}	1.33
β, deg	92.93(6)	R	0.060
V, Å^3	3644(5)	R_w[b]	0.049

[a] Cell parameters were derived by least-squares calculations from angular settings of 25 reflections measured between $6° < 2\theta < 17°$. [b] $R_w = \sum(|F_o - F_c|w^{1/2}/\sum|F_o|w^{1/2}$ and $w = [\sigma^2(F_o)]^{-1}$.

microprobe: Ni:Cl ratio 1:2. Selected IR bands (cm^{-1}): 3450 (H_2O), 3238 (NH), 1606 (py), 1479 (py), 1448 (py), 1086, 625 (ClO_4^-). Molar Conductivity (Λ_m in H_2O): 240 S cm^2 mol^{-1}.

$[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$ (3). To a solution of $[Ni(trenpy)OH_2](ClO_4)_2$ (0.51 g, 1 mmol) in methanol (20 mL) was added NaN_3 (0.032 g, 0.5 mmol) dissolved in a minimum amount of water. The solution was stirred for 1 h and then cooled in an ice bath. The deep purple precipitate that formed was filtered and washed with ethanol and ether (yield: 0.38 g, 82%). Crystals suitable for structure determination were obtained by slow evaporation of an aqueous solution of this product.

Characterization. Calcd for $[Ni_2(C_{12}H_{23}N_5)_2N_3](ClO_4)_3$: C, 30.9; H, 4.9; N, 19.5. Found: C, 30.8; H, 4.7; N, 19.9. Electron Microprobe: Ni:Cl ratio 1:1.5. Selected IR bands (cm^{-1}): 3345, 3300, 3180 (NH), 2080 (N_3), 1609 (py), 1478 (py), 1446 (py), 1084, 625 (ClO_4^-). Molar Conductivity (Λ_m in CH_3CN): 517 S cm^2 mol^{-1}.

$[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$ (4). To a solution of $[Ni(dmptacn)OH_2](ClO_4)_2$ (0.6 g, 1 mmol) in methanol (20 mL) was added NaN_3 (0.032 g, 0.5 mmol) dissolved in the minimum amount of water. The solution was stirred for 1 h and then cooled in an ice bath. The purple precipitate that formed was filtered and washed with ethanol and ether (yield: 0.42 g, 78%).

Characterization. Calcd for $[Ni_2(C_{18}H_{25}N_5)_2N_3](ClO_4)_3$: C, 40.0; H, 4.6; N, 16.9. Found: C, 40.0; H, 4.9; N, 17.1. Electron microprobe: Ni:Cl ratio 1:1.5. Selected IR bands (cm^{-1}): 3314, 3226 (NH), 2078 (N_3), 1606 (py), 1472 (py), 1446 (py), 1090, 625 (ClO_4^-). Molar conductivity (Λ_m in CH_3CN): 525 S cm^2 mol^{-1}.

Crystal Structure Determination. Crystal data and refinement parameters for **3** are given in Table 1. A representative violet tabular crystal of approximate dimensions (0.23 × 0.19 × 0.09 mm) was used for data collection. Intensity measurements were made on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα radiation with $3.5° < 2\theta < 45°$, operating in a ω scan mode with a scan range of 1.30°, at a scan rate between 4.00 and 19.53° min^{-1}. A total of 2401 unique data were collected, ($\pm h,+k,+l$), 1401 of which were considered to be observed [$F \geq 6\sigma(F)$], and used in the final refinement. Three standard reflections monitored every 197 reflections showed no significant variation in intensity over the data collection period. Intensity data were corrected for Lorentz and polarization effects. A face indexed numerical absorption correction was applied[23] on six crystal faces, the maximum and minimum transmission factors being 0.887 and 0.780, respectively. The atomic scattering factors for neutral atoms were taken from ref 24 and were corrected for anomalous dispersion by using values from ref 24. The program used for least-squares refinement was that due to Sheldrick.[23]

The structure was solved by direct methods. Refinement was by full-matrix least-squares employing anisotropic thermal parameters for Ni, Cl, and O and isotropic thermal parameters for all other atoms (single isotropic thermal parameter for hydrogen fixed at 0.08 Å^2—positioned in geometrically idealized positions: C−H 0.96 Å; N−H 0.90 Å). At convergence (151 variables, 1401 observed data) R was 0.060 R_w was 0.049, where $R_w = \sum(|F_o - F_c|w^{1/2}/\sum|F_o|w^{1/2}$ and $w = [\sigma^2(F_o)]^{-1}$. The goodness of fit value $([\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2})$ was 2.24.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^3) for $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$

	x	y	z	U_{iso}[a]
Ni	3983.5(4)	658.9(1.6)	4605.0(8)	28(1)
N(1)	4618(2)	−364(9)	5100(4)	33(2)
N(2)	1/2	0	1/2	28(3)
N(3)	3607(2)	−955(9)	5271(5)	29(2)
N(4)	3331(3)	1469(10)	4219(6)	52(3)
N(5)	4200(3)	2534(10)	3819(5)	35(2)
N(6)	4071(2)	−693(10)	3467(4)	38(2)
N(7)	4098(2)	2375(10)	5623(5)	36(2)
C(1)	3758(3)	−2252(12)	5686(6)	34(3)
C(2)	3459(3)	−3299(13)	6129(6)	45(3)
C(3)	3013(3)	−2867(12)	6154(6)	41(3)
C(4)	2873(3)	−1532(13)	5750(6)	44(3)
C(5)	3157(3)	−611(14)	5279(6)	42(3)
C(6)	3016(3)	900(14)	4809(7)	60(3)
C(7)	3361(4)	3028(14)	3898(8)	73(4)
C(8)	3786(3)	3407(12)	3462(6)	39(3)
C(9)	4452(3)	1784(12)	3107(6)	42(3)
C(10)	4188(3)	362(13)	2740(6)	51(3)
C(11)	4490(3)	3554(12)	4399(6)	42(3)
C(12)	4265(3)	3891(11)	5255(6)	42(3)
Cl(1)	3047(1)	2578(4)	7352(2)	55(1)
O(1)	3120(4)	3228(18)	8159(9)	223(10)
O(2)	3068(5)	1026(14)	7489(9)	198(8)
O(3)	2651(3)	2977(17)	7027(7)	186(8)
O(4)	3394(4)	2963(16)	6925(9)	218(8)
Cl(2)	1/2	3383(5)	3/4	44(2)
O(5)	5018(2)	2415(10)	6724(4)	60(3)
O(6)	4606(3)	4318(12)	7405(5)	102(4)

[a] Equivalent isotropic U for Ni, Cl, and O is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{iso}$ tensor.

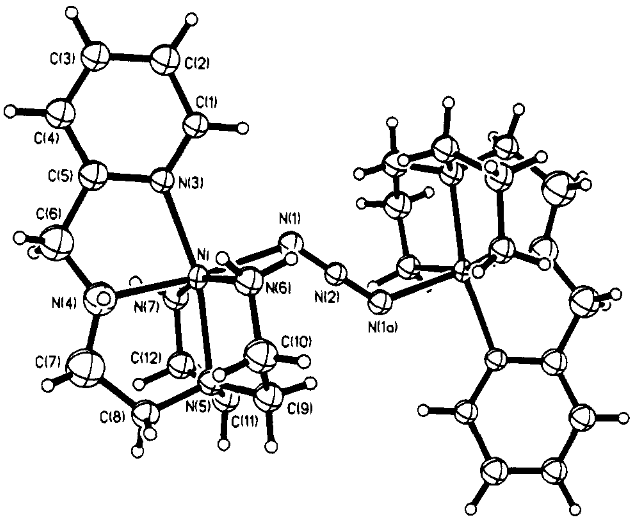

Figure 1. ORTEP drawing and atomic labeling scheme of the $[Ni_2(trenpy)_2(\mu\text{-}N_3)]^{2+}$ cation with 50% thermal ellipsoids.

Final atomic parameters are given in Table 2, with bond lengths and bond angles given in Table 3, and Figure 1 shows the structure of the binuclear cations and the atomic labeling scheme.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer as KBr pellets. The electronic spectra were recorded on a Hitachi 150-20 spectrophotometer. NMR spectra were recorded on a Bruker AC-200 spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS). Low-resolution mass spectra were recorded on a VG TRIO-1 quadrupole mass spectrometer. Electron microprobe analyses were made with a Joel JSM-1 scanning electron microscope through an NEC X-ray detector and pulse processing system connected to a Packard multichannel analyzer. Solid samples were mounted on an aluminium planchet and covered with a very thin film of carbon by using a Balzer Union CED 010 carbon sputterer. Microanalysis were performed by Chemical and Micro-Analytical Services, CMAS, Melbourne, Australia.

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(23) Sheldrick, G. M. SHELXTL PLUS, Revision 3.4, Siemens Analytical Instruments, Inc., Madison, WI, 1988.

(24) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4.

Table 3. Bond Distances and Bond Angles in $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$

Ni−N(1)	2.133 (7)	Ni−N(3)	2.030 (7)
Ni−N(4)	2.070 (8)	Ni−N(5)	2.075 (8)
Ni−N(6)	2.080 (7)	Ni−N(7)	2.111 (8)
N(1)−N(2)	1.168 (7)	N(2)−N(1A)	1.168 (7)
N(3)−C(1)	1.310 (12)	N(3)−C(5)	1.339 (12)
N(4)−C(6)	1.394 (13)	N(4)−C(7)	1.385 (14)
N(5)−C(8)	1.484 (12)	N(5)−C(9)	1.471 (12)
N(5)−C(11)	1.455 (12)	N(6)−C(10)	1.458 (12)
N(7)−C(12)	1.468 (12)	C(1)−C(2)	1.420 (14)
C(2)−C(3)	1.349 (14)	C(3)−C(4)	1.319 (14)
C(4)−C(5)	1.356 (14)	C(5)−C(6)	1.488 (15)
C(7)−C(8)	1.464 (15)	C(9)−C(10)	1.499 (14)
C(11)−C(12)	1.506 (13)	Cl(1)−O(1)	1.342 (15)
Cl(1)−O(2)	1.304 (12)	Cl(1)−O(3)	1.273 (11)
Cl(1)−O(4)	1.269 (14)	Cl(2)−O(5)	1.425 (7)
Cl(2)−O(6)	1.386 (9)	Cl(2)−O(5A)	1.425 (7)
Cl(2)−O(6A)	1.386 (9)		
N(1)−Ni−N(3)	92.5(3)	N(1)−Ni−N(4)	173.4(3)
N(3)−Ni−N(4)	81.0(3)	N(1)−Ni−N(5)	102.5(3)
N(3)−Ni−N(5)	165.0(3)	N(4)−Ni−N(5)	84.1(3)
N(1)−Ni−N(6)	86.3(3)	N(3)−Ni−N(6)	98.5(3)
N(4)−Ni−N(6)	95.2(3)	N(5)−Ni−N(6)	82.9(3)
N(1)−Ni−N(7)	84.9(3)	N(3)−Ni−N(7)	98.7(3)
N(4)−Ni−N(7)	95.5(3)	N(5)−Ni−N(7)	82.6(3)
N(6)−Ni−N(7)	161.0(3)	Ni−N(1)−N(2)	131.6(5)
N(1)−N(2)−N(1A)	180.0(1)	Ni−N(3)−C(1)	127.0(6)
Ni−N(3)−C(5)	114.6(6)	C(1)−N(3)−C(5)	118.4(8)
Ni−N(4)−C(6)	109.5(6)	Ni−N(4)−C(7)	109.2(7)
C(6)−N(4)−C(7)	126.6(9)	Ni−N(5)−C(8)	108.0(5)
Ni−N(5)−C(9)	106.3(6)	C(8)−N(5)−C(9)	111.4(7)
Ni−N(5)−C(11)	105.9(5)	C(8)−N(5)−C(11)	111.7(7)
C(9)−N(5)−C(11)	113.1(7)	Ni−N(6)−C(10)	110.1(6)
Ni−N(7)−C(12)	110.1(5)	N(3)−C(1)−C(2)	121.9(8)
C(1)−C(2)−C(3)	117.7(9)	C(2)−C(3)−C(4)	119.0(10)
C(3)−C(4)−C(5)	122.3(10)	N(3)−C(5)−C(4)	120.5(9)
N(3)−C(5)−C(6)	115.0(9)	C(4)−C(5)−C(6)	124.3(9)
N(4)−C(6)−C(5)	114.6(8)	N(4)−C(7)−C(8)	115.4(9)
N(5)−C(8)−C(7)	114.8(8)	N(5)−C(9)−C(10)	109.7(8)
N(6)−C(10)−C(9)	109.1(7)	N(5)−C(11)−C(12)	111.3(8)
N(7)−C(12)−C(11)	109.5(7)	O(1)−Cl(1)−O(2)	104.3(9)
O(1)−Cl(1)−O(3)	110.2(8)	O(2)−Cl(1)−O(3)	110.7(9)
O(1)−Cl(1)−O(4)	105.6(8)	O(2)−Cl(1)−O(4)	107.2(9)
O(3)−Cl(1)−O(4)	117.9(8)	O(5)−Cl(2)−O(6)	107.2(4)
O(5)−Cl(2)−O(5A)	111.5(7)	O(6)−Cl(2)−O(5A)	109.6(4)
O(5)−Cl(2)−O(6A)	109.6(4)	O(6)−Cl(2)−O(6A)	112.0(8)
O(5A)−Cl(2)−O(6A)	107.2(4)		

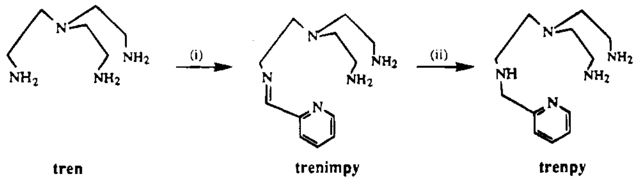
Conductance measurements were made on a Crison 522 Conductimeter with Pt black electrodes at a concentration of 10^{-3} M.

Magnetic susceptibility measurements were carried out on polycrystalline samples in the temperature range 4.2−300 K on a Quantum Design MPMS SQUID magnetometer. The samples were contained in gelatin capsules which were held in the center of a soda straw fused to the end of the sample rod.

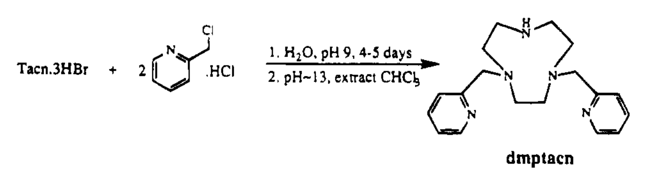
Results and Discussion

Preparation of Ligands and Metal Complexes. Reaction of equimolar amounts of tren with pyridine-2-carboxyaldehyde, in either methanol or water, produces the one-to-one Schiff base adduct trenimpy, which on reduction with borohydride produces the pentadentate ligand trenpy (Scheme 1). The ^{13}C NMR spectrum of the ligand indicated that some di- and trisubstituted derivatives are also formed. For convenience, the synthesis of Ni(II) complexes was achieved by reacting an unpurified aqueous solution of the ligand with an equimolar amoumt of a Ni(II) salt. Pure solutions of the desired product, $[Ni(trenpy)OH_2]^{2+}$, were obtained following cation exchange chromatography. Evaporation gave pink crystals with composition $[Ni(trenpy)OH_2](ClO_4)_2{\cdot}H_2O$.

Scheme 1. Synthesis of trenpy: (i) Pyridine-2-carboxyaldehyde, MeOH; (ii) $NaBH_4$



Scheme 2. Synthesis of dmptacn



The synthesis of dmptacn involved reaction of an aqueous solution of tacn·3HBr with picolylchloride·HCl at pH = 9 (Scheme 2). Control of solution pH was important since at higher pH the product contained considerable proportions of the trisubstituted product, tmptacn, whose coordination chemistry has been previously explored.[25] ^{13}C and ^{1}H NMR data were consistent with the proposed structure of the ligand, but there was evidence for the presence of small amounts of tmptacn. The ligand was found to be hygroscopic and satisfactory elemental analyses could not be obtained. The ligand analysed satisfactorily after conversion to the tetrahydrobromide salt, dmptacn·4HBr. The dmptacn complex, $[Ni(dmptacn)OH_2](ClO_4)_2{\cdot}H_2O$, was obtained on addition of sodium perchlorate to a solution containing equimolar amounts of the ligand and Ni^{2+}. Elemental and electron microprobe analyses were consistent with the given compositions. The IR spectra contained N−H stretching frequencies in the region 3160−3450 cm^{-1}, bands due to the pyridines at about 1610, 1480, and 1450 cm^{-1} and bands due to perchlorate counterions at 1090 and 625 cm^{-1}.

Two azido-bridged binuclear nickel complexes (**3** and **4**) were prepared by evaporating dilute aqueous solutions containing the respective mononuclear complexes and sodium azide in a 1:2 ratio. Elemental analyses, electron microprobe, and molar conductivity measurements all indicated that the complexes were binuclear in nature having the compositions $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$ and $[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$. The IR spectra of the two binuclear complexes contain one band due to asymmetric stretching of the bridging azide (ν_{as} 2080 cm^{-1}) in addition to bands due to the corresponding ligands (also observed in the mononuclear complexes) and the perchlorate counterions.

Crystal Structure. The molecular structure of **3** consists of discrete $[(trenpy)Ni\text{-}N_3\text{-}Ni(trenpy)]^{3+}$ binuclear cations which are held together by a single azido bridging group coordinated in a μ-1,3 or end-to-end fashion (Figure 1). To our knowledge, $[Ni_2(Me_4cyclam)_2(N_3)_2](\mu\text{-}N_3)](ClO_4)_3$,[7,26] is the only other binuclear Ni(II) complex with a single azide bridge. The geometry about each Ni(II) center is pseudooctahedral with five coordination sites occupied by the chelating trenpy ligand and the end nitrogen (N(1)) of the bridging azide group completing the coordination sphere. The μ-1,3 coordination of the azide group is encouraged by steric effects introduced by the trenpy ligand and results in a crystallographic center of inversion at

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(25) (a) Christiansen, L.; Hendrickson, D. N.; Toftlund, H.; Wilson, S. R.; Xie, C.-L. *Inorg. Chem.* **1986**, *25*, 2813. (b) Wieghardt, K.; Schöffmann, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877.

(26) Wagner, F.; Mocella, M. T.; D'Aniello, M. J., Jr.; Wang, A. H.-J.; Barefield, A. *J. Am. Chem. Soc.* **1974**, *96*, 2625.

the central azide nitrogen. The centrosymmetric nature of **3** means that the Ni−NNN−Ni torsion angle is 180°. The arrangement of the ligand in the cation is similar to that observed in other tren-based ligands, (e.g. $[Cu(trenen)]^{2+}$,[27] $[Cu(trenpy)]^{2+}$,[28] $[Co(trenen)-O_2-Co(trenen)]^{4+}$,[11] $[Co(trenenim)Cl]^{2+}$,[12] and $[Co(trenen)Cl]^{2+}$ [13]). The azide group in $[(trenpy)Ni-N_3-Ni(trenpy)]^{3+}$ is situated *trans* to the secondary amine; the same position is occupied by the chloro and peroxo groups in the Co(III) complexes of tren-based ligands. The secondary nitrogen appears to be more effective at inducing *trans* coordination than the tertiary nitrogen present in these types of ligands.[11−13] The stereochemistry of the ligand dictates that the azide is *trans* to either the secondary or the tertiary nitrogen. In the complex, the extended ligand arm contains the pyridyl nitrogen N(3), the secondary nitrogen N(4), and the tripodal nitrogen N(5) coordinates meridional to the Ni(II) center in preference to facial coordination which would place the azide *trans* to the tertiary nitrogen.

The Ni−N(4), −N(5), −N(6), and −N(7) bond distances (2.07−2.11 Å, Table 3) are typical of Ni−N distances found in many other nickel amine complexes. A compilation of structural data for Ni(II) amine complexes gives the average Ni−N distances for primary, secondary, and tertiary amines as 2.097(24), 2.097(42), and 2.144(57) Å, respectively.[29] The uncertainties in each of these values indicate considerable variation from complex to complex. However, it is worthwhile noting that the Ni−N bond distance to the tertiary amine nitrogen in **3** of 2.075(8) Å is shorter than in many other cases.[29] This has also been observed in related Ni(II)−tren complexes such as $[Ni(tren)(\mu\text{-}N_3)_2Ni(tren](B(C_6H_5)_4)_2$ [7] and $[Ni(tren)(NCS)_2]$.[30] A further feature of these complexes also evident in **3** is that one Ni−N(primary) distance (Ni−N(7) in **3**) is consistently longer than the others. The Ni−N(3) distance, 2.030(7) Å, is shorter than typical Ni−N(py) bond lengths because the pyridine ring forms part of a chelate ring. Shorter Ni−N bond lengths are commonly found in phenanthroline and bipyridine complexes of Ni(II). The Ni−N(1) distance (2.133(7) Å) is typical of Ni−N(bridging azide) bond lengths. The angles around the tertiary nitrogen N(5)−Ni−N(*i*) (*i* = 4,6,7) are acute (average 83.2(3)°) and result in considerable deviation from idealized tetragonal geometry, as is often seen in complexes of ligands with 5-membered chelate rings. However, the Ni−N(1)−N(2) angle of 131.6° is in the normal range for azido-bridged nickel(II) amine complexes (120−142°). The opening up of the angle (>120°) results from unfavorable steric interactions between the (puckered) ethyl groups linking the nitrogens *cis* to the bridging azide on each nickel. There are two such linkages in **3** compared with four in $[Ni_2(Me_4cyclam)_2(N_3)_2]\text{-}(\mu\text{-}N_3)](ClO_4)_3$ (angle 142°).[7,26]

Table 4. Electronic Spectra for Complexes 1−4

compound	solvent	λ_{max}, nm (ϵ_{max}, $M^{-1}\,cm^{-1}$)
$[Ni(trenpy)(H_2O)](ClO_4)_2\cdot H_2O$	H_2O	547 (10.1), 795 (17.7), 900 (19.8)
	CH_3CN	527 (14.4), 806 (20.1), 848 (21.0)
$[Ni(dmptacn)(H_2O)](ClO_4)_2\cdot H_2O$	H_2O	523 (15.6), 807 (20.3), 865 (21.0)
	CH_3CN	516 (17.7), 800 (28.3), 880 (22.3)
$[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$	CH_3CN^a	542 (13.9), 820 (23.0), 875 (25.1)
$[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$	CH_3CN^a	531 (15.7), 821 (22.6), 888 (20.3)

[a] ϵ values are given per Ni(II) center.

Electronic Spectra. UV−vis spectral data for complexes **1**−**4** are summarized in Table 4. Spin allowed d−d transitions are observed in the 800−900 and 500−550 nm regions, as expected for Ni(II) complexes.[31,32] However, a third d−d transition expected in the 300−400 nm region is masked by a $\pi \rightarrow \pi^*$ transition within the pyridine rings and/or M → L charge transfer bands. The band in the 800−900 nm region is asymmetric, as is the case for $[Ni(tacn)_2]^{2+}$,[33−35] $[Ni(tmptacn)]^{2+}$ (tmptacn = 1,4,7-tris(2-methylpyridyl)-1,4,7-triazacyclononane),[25b] $[Ni\{(pz)_3CH\}_2]^{2+}$ ($CH(pz)_3$ = tris(pyrazol-1-yl)methane)[36,37] and a variety of other Ni(II) complexes.[32] This can be attributed to the presence of the ${}^3A_{2g} \rightarrow {}^1E_g$ spin forbidden transition and to the asymmetry in ligand field of trenpy and dmptacn which causes splitting of the ${}^3T_{2g}$ state. Stranger *et al.*[35] have carried out detailed ligand field analysis (using the angular overlap model) of the single crystal absorption spectrum of $[Ni(tacn)_2]^{2+}$ and have concluded that one of the spin−orbit components of the ${}^3T_{2g}$ state mixes with the ${}^1E_g$ state. This gives rise to an increase in the intensity of the ${}^3A_{2g} \rightarrow {}^1E_g$ transition. Full assignment of the spectra of **1**−**4** requires single-crystal absorption spectra and curve fit analysis, such as those carried out by Stranger, Gahan, and co-workers,[35,38] but at the present time suitable crystals have not been obtained. In the absence of this some general conclusions can be made: (i) the dmptacn complexes have bands at higher energy than the trenpy complexes, indicating that dmptacn induces greater crystal field splitting; (ii) for both ligands, the band energy follows the order $H_2O < N_3^- < CH_3CN$ indicating that greater splitting is caused by N rather than O donors; (iii) for the dmptacn complexes, the N_3^- and CH_3CN complexes show crystal field splitting similar to that of $[Ni(tacn)_2]^{2+}$ [33−35] and $[Ni(tmptacn)]^{2+}$,[25b] both of which have NiN_6 chromophores.

Magnetic Properties. The solid-state magnetic susceptibilities of **3** and **4** were measured at 10 kG and in the temperature range 4.2−300 K. Plots of molecular susceptibility, χ_{Ni} against temperature are shown in Figures 2 and 3. For both complexes, χ_{Ni} increases as temperature decreases, reaching a maximum at ~75 K for **3** and 125 K for **4** and then decreases reaching a minimum at temperatures below 20 K. The small rise at very low temperatures is attributable to small amounts of paramagnetic impurities. Plots of μ_{Ni} versus temperature, which are equivalent to $\chi_{Ni}T$ versus T, are also shown in Figures 2 and 3. The μ_{Ni} values are reduced a little from the normal monomer value at 290 K and they decrease gradually towards 0.4 μ_B at 4.2 K. This behavior is typical of weak to medium antiferromagnetic coupling between pairs of Ni(II) centers which is mediated by the azide bridges. Experimental data have been fitted by linear least-squares methods to the following suscep-

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(27) Cannas, M.; Christini, A.; Marongiu, G. *Inorg. Chim. Acta* **1976**, *19*, 241.

(28) McLachlan, G.; Spiccia, L. Manuscript in preparation.

(29) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem Soc., Dalton Trans.* **1989**, S1.

(30) Santarsiero, B. D.; Schomakev, V. *Acta Crystallogr.* **1983**, *C39*, 1216.

(31) (a) Sutton, D. *Electronic Spectra of Transition Metal Complexes*; McGraw-Hill: London, 1968. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, England, 1984.

(32) Hart, S. M.; Boeyens, J. C.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 982.

(33) Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499.

(34) Reinen, D.; Ozarowski, A.; Jakob, B.; Pebler, J.; Stratemeier, H.; Wieghardt, K.; Tolksdorf, I. *Inorg. Chem.* **1987**, *26*, 4010.

(35) Stranger, R.; Wallis, S. C.; Gahan, L. R.; Kennard, C. H. L.; Byriel, K. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2971.

(36) Astley, T.; Canty, A. J.; Hitchman, M. A.; Rowbottom, G. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 1981.

(37) Astley, T.; Gulbis, J. M.; Hitchman, M. A.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1993**, 509.

(38) Donlevy, T. M.; Gahan, L. R.; Stranger, R.; Kennedy, S. E.; Byriel, K. A.; Kennard, C. H. L. *Inorg. Chem.* **1993**, *32*, 6023.

Table 5. Structural and Magnetic Data for Azido-Bridged Nickel Complexes

compound	J,[a] cm^{-1}	Ni−N−N angle, deg	Ni−N(azide), dist, Å	Ni••Ni dist, (Å)	torsion angle, deg	ref
$[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$	−26.8	131.6	2.133(7)	6.07	0	this work
$[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$	−42.5					this work
catena-$[Ni(cyclam)(\mu\text{-}N_3)](ClO_4)$[b]	−19.6	140.7 128.2	2.165(3) 2.172(4)	6.15	13.1	18
$[Ni_2(Me_4cyclam)_2(N_3)_2(\mu\text{-}N_3)]ClO_4$[c]	−12.3	142	2.15(1)	6.12	0	7
catena-$[Ni(232\text{-}tet)(\mu\text{-}N_3)](ClO_4)$[d]	−13.5	134.6 124.1	2.151(4) 2.156(4)	5.95	37.6	21
catena-$[Ni(323\text{-}tet)(\mu\text{-}N_3)](ClO_4)$[e]	−31.4	135.8 119.8	2.129(4) 2.181(4)	5.96	10.7	21

[a] All values are based on a $-2J\ \hat{S}_1\cdot\hat{S}_2$ Hamiltonian. [b] cyclam = 1,4,8,11-tetraazacyclotetradecane. [c] Me$_4$cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. [d] 232-tet = *N,N′*-bis(2-aminoethyl)-1,3-propanediamine. [e] 323-tet = *N,N′*-bis(2-aminopropyl)-1,2-ethanediamine.

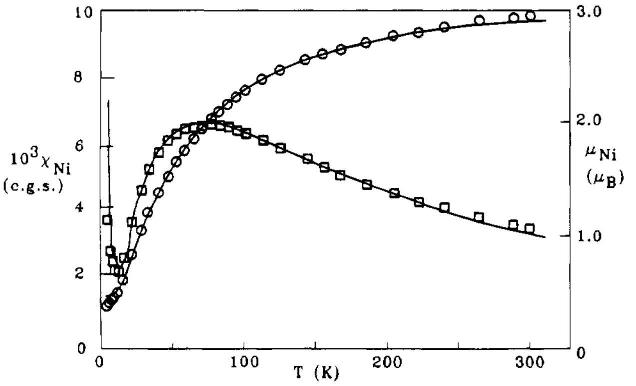

Figure 2. Experimental and calculated (solid line) temperature dependence of the molar magnetic susceptibility (□) and magnetic moment (○) of $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$. The parameters used to calculate the solid lines are given in the text.

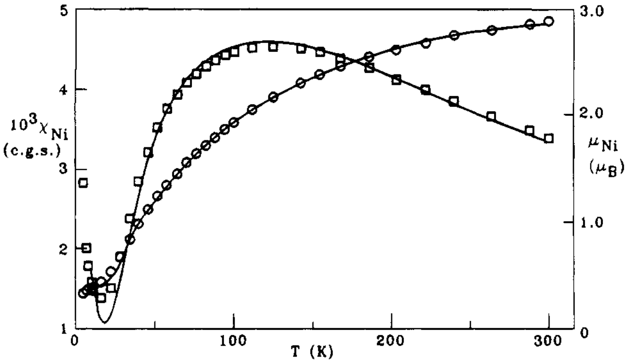

Figure 3. Experimental and calculated (solid line) temperature dependence of the molar magnetic susceptibility (□) and magnetic moment (○) of $[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$. The parameters used to calculate the solid lines are given in the text.

tibility expression for an $S = 1$ dimer which allows for a fraction, x, of $S = 1$ monomeric "impurity".

$$\chi_m(\text{per Ni}) = (1 - x)\frac{N\beta^2g^2}{kT}(\exp(-4J/kT) + 5)/(\exp(-6J/kT) + 3\exp(-4J/kT) + 5) + 2xN\beta^2g^2/3kT$$

The value of x was 0.02 for **3** and 0.012 for **4**. The analysis gave the values of the exchange coupling parameter, J, as −26.8 cm^{-1} and a g value of 2.24 for **3**. The corresponding values for **4** were $J = -42.5$ cm^{-1} and a g value of 2.36. The data are summarized in Table 5 together with data for other related azide bridged Ni(II) complexes.

The J values for complexes **3** and **4** are in the normal range for singly bridged Ni(II) azide complexes (see Table 5). The magnitude of the coupling in $[Ni_2(trenpy)_2(\mu\text{-}N_3)](ClO_4)_3$ is about twice that of the related singly bridged complex, $[Ni_2(Me_4cyclam)_2(N_3)_2(\mu\text{-}N_3)](ClO_4)$[7] ($J = -26.8$ *vs* -12.3 cm^{-1}). Several factors have been suggested[20,21] as important in determining the strength of coupling in end-to-end azido-bridged dinickel compounds: the Ni(II)−N$_3$−Ni(II) torsion angle, the Ni−N (azide) bond angles and lengths, and the electronic states of the Ni(II) centers. The greater coupling in **3** cannot be attributed to a change in torsion angle (0° in both complexes) or in the Ni−N(azide) bond length (2.15(1) Å for the Me$_4$cyclam complex and 2.133(7)Å for **3**) and but is probably due to a decrease Ni−N−N(azide) bond angle from 142° in the Me$_4$-cyclam complex to 131.6° in **3**. Magneto−structural correlations by Escuer *et al.*[21] have concluded that the strength of interaction between Ni(II) centers in complexes with single azide bridges increases as the Ni−N−N angle decreases towards 120°. There is also a slight difference in the Ni••Ni separation for these complexes (6.07 Å for **3** and 6.12 Å for the Me$_4$cyclam complex) but there are not enough data to ascertain the relative importance of this factor. Three one-dimensional polynuclear nickel complexes, in which the Ni(II) centers are linked exclusively by singly bridging azido groups in the μ-1,3 mode, have been reported (see Table 5). All these complexes are not centrosymmetric, thus making correlations of exchange interactions difficult. This asymmetry gives rise to two Ni−N−N bond angles (and in one case to two distinctly different Ni−N bond distances) and a nonzero torsion angle within each Ni−N$_3$−Ni bridging moiety. Both *catena*-$(\mu\text{-}N_3)[Ni(cyclam)](ClO_4)\cdot H_2O$[18] and *catena*-$(\mu\text{-}N_3)[Ni(232\text{-}tet](ClO_4)$,[21] where 232-tet = *N,N′*-bis(2-aminoethyl)-1,3-propanediamine, exhibit exchange interactions similar to those of **3**. In the latter case, the more effective overlap that is expected because of a smaller Ni−N−N angle is offset by a high torsion angle of 37.6°. In contrast, *catena*-$(\mu\text{-}N_3)[Ni(323\text{-}tet](ClO_4)$, where 323-tet = *N,N′*-bis(2-aminopropyl)-1,2-ethanediamine, has a low torsion angle and one small Ni−N−N angle and exibits much stronger coupling.[21] MO calculations have shown that the strength of the interaction decreases significantly as the torsion angle increases 10−15° to 50°. The foregoing discussion suggests that the higher J value for $[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$ compared with **3** results primarily from a decrease in Ni−N−N angle.[21] This decrease would be greater if the torsion angle for this complex is greater than that of **3**.

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Supplementary Material Available: Tables of anisotropic displacement coefficients, H-atom coordinates and isotropic displacement coefficients for **3** (2 pages). Ordering information is given on any current masthead page.