Indian Journal of Chemistry
Vol. 42A, May 2003, pp. 1004-1007

Synthesis, X-ray crystal structure and magnetic properties of a new binuclear complex derived from a pentadentate Schiff base ligand

Soma Deoghoria[a], W T Wong[b] & Swapan K Chandra*[a]

[a]Department of Chemistry, The University of Burdwan, Burdwan 713 104, India, e-mail: dr_swapan@sify.com

[b]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

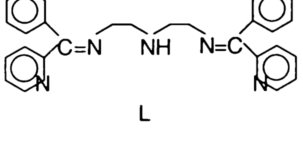
Received 5 September 2002; revised 16 January 2003

A new binuclear nickel(II) complex $[Ni_2L_2(N_3)_2](ClO_4)_2$ **1** has been synthesized and characterized. The structure of **1** has been determined by single crystal X-ray diffraction studies. The structure analysis indicates that each nickel(II) centre is in a distorted octahedral (NiN_6) coordination environment with three nitrogen atoms from one and two nitrogen atoms from other pentadentate ligand and the last one from terminal azido ion. Variable-temperature magnetic susceptibility measurements of the compound **1** showed no evidence of magnetic exchange between two nickel(II) centres. This is consistent with the structure with large Ni...Ni distance (5.865(1) Å) and absence of any suitable bridging ligand capable of transmitting this type of interactions.

The coordination properties of bi- and polynuclear nickel(II) complexes have received considerable attention in recent years. The investigation of magnetic behaviour of these complexes and correlating with their structures is important in the area of molecular magnetism[1-5]. Flexible polydentate ligands[6] and/or suitable bridging anions[7] are excellent instrument for assembling more than one metal centres in reasonably close proximity for magnetic exchange interactions. The pseudohalide anions (N_3^-, NCS^-, NCO^-) have been known for their numerous ligating abilities leading to variety of coordination species[8]. It is also well established that end-on and end-to-end bridging coordination mode favours respectively ferromagnetic[9] and antiferromagnetic[10] interactions. Herein we describe synthesis, single crystal X-ray structure and magnetic properties of a binuclear nickel(II) complex $[Ni_2L_2(N_3)_2](ClO_4)_2$ **1** derived from a flexible pentadentate Schiff base ligand through an unusual[11] bridging mode of this type of linear pentadentate ligand and azide ion acting as a terminal donor.

Materials and Methods

Diethylene triamine, 2-benzoyl pyridine and sodium azide were purchased from Lancaster Chemical Company Inc. and used as received. All other solvents and chemicals were of analytical grade. The pentadentate ligand (L) was prepared as reported previously and gave satisfactory elemental analysis[12].



L

Preparation of $[Ni_2L_2(N_3)_2](ClO_4)_2$ **1**

To an warm acetonitrile solution (5 cm^3) of $Ni(ClO_4)_2.6H_2O$ (0.183 g, 0.5 mmol) was added 0.217 g (0.5 mmol) of ligand (L) in 10 cm^3 acetonitrile. To the resulting brown-red solution an aqueous solution of sodium azide (0.034 g, 0.5 mmol, 2 cm^3 H_2O) was added slowly with constant stirring. The clear red solution was left for slow evaporation and after 3-4 days deep red needle crystals of **1** were obtained. Yield: 0.140 g, 44% (Anal.: Found : C, 52.9; H, 4.4; N, 17.5; Ni, 9.1. Calcd. for $C_{56}H_{54}N_{16}O_8Cl_2Ni_2$: C, 53.1; H, 4.3; N, 17.7, Ni, 9.3%.

CAUTION: Perchlorate salts and azido complexes are potentially explosive especially in presence of organic ligands. Therefore, preparation and handling of these compounds deserve special attention.

Elemental analysis for carbon, hydrogen and nitrogen were performed using a Perkin Elmer 2400II elemental analyzer. Nickel contents was determined by atomic absorption spectrophotometric measurements (A GBC Model-Avanta was used). Variable temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID spectrophotometer. Pascal's constants were utilized to estimate diamagnetic correction, this value was subtracted from the experimental susceptibility data to give molar magnetic susceptibility (χ_M). The IR spectra (4000-400 cm^{-1}) were taken in KBr discs at 298 K using JASCO FT/IR-420 spectrometer.

Crystal structure determination and refinement

A suitable crystal of **1** was mounted on a Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromated M_oK_α radiation. The unit

Table 1—The crystal data and data collection summary for $[Ni_2L_2(N_3)_2](ClO_4)_2$ **1**

Empirical formula	$C_{56}H_{54}N_{16}O_8Cl_2Ni_2$
Formula Weight	1267.43
Space group	$P2_1/n$ (no. 14)
a (Å)	8.7850(5)
b (Å)	15.7670(9)
c (Å)	20.2120(10)
α (°)	90
β (°)	90.550(10)
γ (°)	90
V (Å^3)	2799.5(3)
Z	2
ρ_{calcd} (g cm^{-3})	1.504
F(000)	1312
Crystal size (mm)	0.21 × 0.19 × 0.19
μ (M_o Kα) (mm^{-1})	0.839
λ (Å)	0.71069
Temperature (K)	298
$2\theta_{max}$ (°)	55.0
Reflections collected	17482
Independent reflections	6511 (R_{int} = 0.021)
Reflections observed [I > 1.5σ(I)]	4618
Goodness-of-fit	1.43
R^a; wR^b	0.0472; 0.0540

Largest difference peak and hole (e Å^{-3})0.57 and -0.41

$^a R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$;

$^b wR = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 2 — Selected bond distances (Å) and bond angles (°) for the compound $[Ni_2L_2(N_3)_2](ClO_4)_2$ **1**

Bond distances			
Ni(1)-N(1)	2.0200(16)	Ni(1)-N(2)	2.174(3)
Ni(1)-N(3)	2.091(3)	Ni(1)-N(4)	2.0789(16)
Ni(1)-N(5)	2.090(2)	Ni(1)-N(6)	2.088(2)
N(6)-N(7)	1.189(4)	N(7)-N(8)	1.157(4)
C(1)-N(1)	1.462(4)	C(5)-N(1)	1.282(4)
Bond angles			
N(1)-Ni(1)-N(2)	80.65(8)	N(1)-Ni(1)-N(3)	78.09(11)
N(1)-Ni(1)-N(4)	177.26(9)	N(1)-Ni(1)-N(5)	99.25(8)
N(1)-Ni(1)-N(6)	89.98(11)	N(2)-Ni(1)-N(3)	158.75(10)
N(2)-Ni(1)-N(4)	98.65(7)	N(2)-Ni(1)-N(6)	89.23(9)
N(3)-Ni(1)-N(4)	102.58(10)	N(3)-Ni(1)-N(5)	90.27(9)
N(3)-Ni(1)-N(6)	90.82(10)	N(4)-Ni(1)-N(5)	78.11(7)
N(4)-Ni(1)-N(6)	92.67(10)	N(5)-Ni(1)-N(6)	170.73(10)
N(6)-N(7)-N(8)	179.4(3)		

cell parameters were determined by the least-squares refinement of setting angles of 25 reflections. Intensity data were collected in the ω-2θ scan mode. The data were corrected for Lorentz and polarization effects[13]. The structure was solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using teXsan[14] crystallographic software package of Molecular Structure Corporation. The crystal data and data collection details are collected in Table 1.

Results and Discussion

Synthesis

The ligand was reacted with nickel(II) perchlorate hexahydrate and sodium azide using a ratio of L : Ni^{II} : N_3^- = 1 : 1 : 1 in aqueous acetonitrile medium affording red crystalline product suitable of X-ray crystallographic work having composition $[Ni_2L_2(N_3)_2](ClO_4)_2$. It is also interesting to note that by changing ratio of L : Ni^{II} : N_3^- = 1 : 1 : 0.5 which is usual ratio to make binuclear compound of the usual type $[Ni_2L_2(N_3)]^{3+}$ lead to the same compound **1**. The complex **1** was insoluble in all common solvents.

The IR spectrum of **1** exhibits a very strong absorption at 2028 cm^{-1} that corresponds to the asymmetric stretching vibrations of azide and the stretching vibrations of C=N bond of Schiff base at 1637 and 1588 cm^{-1} (ref. 15).

Crystal structure of $[Ni_2L_2(N_3)_2](ClO_4)_2$ **1**

The ORTEP drawing of the dimeric cation $[Ni_2L_2(N_3)_2]^{2+}$ of **1** is shown in Fig. 1, and the selected bond distances and angles are listed in Table 2. Each nickel(II) is in a distorted octahedral (NiN_6) coordination environment consisting of three nitrogen atoms from one, two nitrogen atoms from another pentadentate ligand and the last one from terminal azido ion. In this molecule each flexible ligand shows a very unusual[11] type of binding mode and distributed its coordination potential to two different nickel(II) centres thereby forms the dimer. The Ni-N distances are ranging from 2.0200(16) to 2.174(3) Å for complex **1**. These Ni-N distances are consistent with corresponding values of analogous NiN_6 chromophores[1b, 7, 16]. The Ni1...Ni1a separation is 5.865(1) Å. The *cis* and *trans* angles vary from 78.09(11) to 102.58(10) and 158.75(10) to 177.26(9)° respectively, indicating the nature of distortion in the coordination sphere.

Variable-temperature magnetic susceptibility study was performed on polycrystalline sample of **1**. The magnetic susceptibility (χ_M) of this compound was

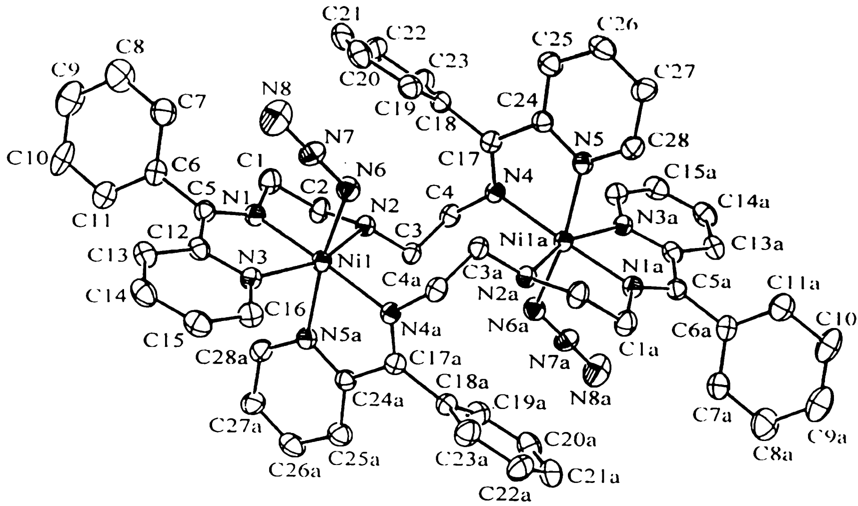


Fig. 1—ORTEP plot and labeling scheme for $[Ni_2L_2(N_3)_2]^{2+}$. For clarity the hydrogen atoms are not shown.

examined in a 10.0 kG field in the temperature range 2.0-300.0 K. Variable-temperature magnetic susceptibility data showed no evidence of coupling between the two paramagnetic nickel(II) centres. In compound **1** the large intramolecular separation (5.865(1) Å) and bridged by the pentadentate ligand that involved a long pathway for magnetic exchange and also saturated links ($-CH_2-CH_2-$) in the ligand are indicative that this complex to be paramagnetic in behaviour[17]. It's magnetic moment of 2.89 B.M./Ni, which is close to spin-only value for $S = 1$, is almost constant over the temperature range of 300 to 25 K and then decreases due to zero-field splitting and intermolecular interactions. As a result the fitting of magnetic data to get reasonable value of exchange parameters was not possible. This result is perfectly consistent with the crystal structure (*vide supra*).

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 172530. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax : 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgement

The project was financially supported by the Council of Scientific and Industrial Research and University Grants Commission (under DSA program), New Delhi, India. One of the authors (S D) is thankful for the fellowship provided by The University of Burdwan. We are also grateful to Prof. A K Das and Mr. B C Mondal of our department for their kind help regarding atomic absorption data. The authors are indebted to Prof. G Christou and Dr. M Soler for the magnetic results.

References

1 (a) Barandika M G, Cortes R, Lezama L, Urtiaga M K, Arriortua M I & Rojo T, *J Chem Soc, Dalton Trans*, (1999) 2971; (b) Arriortua M I, Cortes R, Lezama L, Rojo T, Solans X & Font-Bardia M, *Inorg Chim Acta*, 174 (1990) 263; (c) Escuer A, Vicente R & Ribas J, *J Magn Magn Mater*, 110 (1992) 181; (d) Escuer A, Vicente R, Ribas J & Solans X, *Inorg Chem*, 34 (1995) 1793; (e) Escuer A, Vicente R, El Fallah M S, Solans X & Font-Bardia M, *Inorg Chim Acta*, 247 (1996) 85; (f) Cortes R, Ruiz de Larramendi J I, Lezama L, Rojo T, Urtiaga M K & Arriortua M I, *J Chem Soc, Dalton Trans*, (1992) 2723; (g) Vicente R, Escuer A, Ribas J, El Fallah M S, Solans X & Font-Bardia M, *Inorg Chem*, 32 (1993) 1920; (h) Ribas J, Monfort M, Diaz C, Bartos C & Solans X, *Inorg Chem*, 33 (1994) 484.

2 Pierpont C G, Hendrickson D N, Duggana D M, Wagner F & Barefield E K, *Inorg Chem*, 14 (1975) 604; Chaudhuri P, Guttman M, Ventur D, Weighardt K, Nuber B & Weiss J, *J Chem Soc, Chem Comm*, (1985) 1618; Escuer A, Castro I, Mautner F, El Fallah M S & Vicente R, *Inorg Chem*, 36 (1997) 4633; Ribas J, Monfort M, Ghosh B K, Cortes R, Solans X & Font-Bardia M, *Inorg Chem*, 35 (1996) 864; Escuer A, Vicente R, El Fallah M S, Solans X & Font-Bardia M, *Inorg Chim Acta*, 278 (1998) 43.

3 Monfort M, Resino I, Ribas J, Solans X, Font-Bardia M, Rabu P & Drillon M, *Inorg Chem*, 34 (2000) 2572; Escuer A, Vicente R, El Fallah M S, Kumar S B, Mautner F A & Gatteschi D, *J Chem Soc, Dalton Trans*, (1998) 3905.

4 Maji T K, Laskar I R, Mostafa G, Welch A J, Mukherjee P S & Chaudhury N R, *Polyhedron*, 20 (2001) 651 and references cited therein.

5 Kahn O, *Molecular Magnetism*, VCH, New York (1993); Gatteschi D, Kahn O, Miller J S & Palacio F, *Magnetc Molecular Materials*, NATO ASI, Kluwer, Dordrecht (1991).

6 Dapporto P, Formica M, Fusi V, Mivchaloni M, Paoli P, Pontellini R & Rossi P, *Inorg Chem*, 39 (2000) 4663.

7 Ribas J, Monfort M, Diaz C, Bartos C & Solans X, *Inorg Chem*, 32 (1993) 3557.

8 Vrieze K & Van Koten G, *Comprehensive Coordination Chemistry*, Wilkinson G, Gillard R D & Mcleverty J A, Eds, Pergamon Press, Oxford, England (1987), vol 2, p225 and references therein.

9 Ruiz E, Cano J, Alvarej S & Alemany P, *J Am Chem Soc*, 120 (1998) 11122.

10 De Biani F F, Ruiz E, Cano J, Novoa J J & Alvarej S, *Inorg Chem*, 39 (2000) 3221.

11 Vaira M D, Mani F & Stoppioni P, *Inorg Chim Acta*, 303 (2000) 61.

12 Deoghoria S, Sain S, Moulton B, Zaworotko M J, Bera S K & Chandra S K, *Polyhedron*, 21 (2002) 2457.

13 North A C T, Phillips D C & Mathews F S, *Acta Crystallogr*, Sect A 24 (1968) 351.

14 teXsan : *Crystal Structure Analysis Package*, Molecular Structure Corporation (1985 & 1992) .

15 Nakamoto K, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1997).

16 Laskar I R, Maji T K, Chaudhuri S, Ghosh A & Chaudhuri N R, *Polyhedron*, 19 (2000) 1803.

17 Brudenell S J, Spiccia L, Bond A M, Fallon, Hockless D C R, Lazarev G, Mahon P J & Tiekink E R T, Inorg Chem 39 (2000) 881.