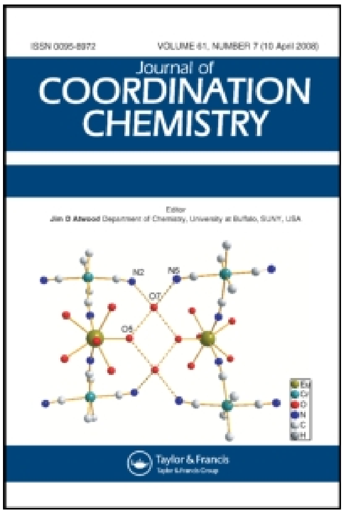

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Adhikary, Chandan , Mal, Dasarath , Chaudhuri, Siddhartha and Koner, Subratanath(2006) 'Synthesis, characterisation and X-ray structure of an azido adduct of a tridentate (NNO) Schiff base nickel(II) complex', Journal of Coordination Chemistry, 59: 7, 699 — 704

To link to this Article: DOI: 10.1080/00958970500266024

URL: http://dx.doi.org/10.1080/00958970500266024

Journal of Coordination Chemistry
Vol. 59, No. 7, 10 May 2006, 699–704

Synthesis, characterisation and X-ray structure of an azido adduct of a tridentate (NNO) Schiff base nickel(II) complex

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(*Received 14 June 2005; in final form 15 July 2005*)

The tridentate Schiff base 1-(*N*-salicylideneimino)-2-(*N*,*N*-diethyl-aminoethane (HL), derived from the condensation of salicylaldehyde with *N*,*N*-diethylethylenediamine, reacted with nickel(II) nitrate and azide to give a mononuclear complex of formula $[Ni(L)(N_3)]$, where $HL = Et_2N(CH_2)_2NCHC_6H_4(OH)$. The complex was characterized by spectroscopic and X-ray crystallographic methods. Coordination around nickel(II) is square planar. The molecular and supramolecular structure of the complex is discussed.

Keywords: Nickel(II); Azide; Tridentate Schiff base; Synthesis; Crystal structure

1. Introduction

Complexes of copper(II) with tridentate *N*-alkylidene or *N*-arylidene alkanato Schiff bases are of considerable interest due to their structural and magnetic properties, and their potential as models for a number of important biological systems [1]. Several *N*-salicylideamino alkanato complexes exhibit antimicrobial, anti-inflammatory and antipyretic activities [2], together with activity similar to superoxide dismutase [3]. Various NNO and NNN donor tridentate Schiff bases are reported in the literature, in which all three donor sites coordinate to a metal ion [4]. The flexibility of the coordination sphere of copper(II) allows it to adopt various stereochemical arrangements. Despite the fact that a substantial array of copper(II) azido complexes of tridentate NNO or NNN Schiff base ligands have been synthesized [5], nickel(II) analogues have received little attention [6]. In an attempt to synthesize azido-bridged polynuclear nickel(II) complexes containing tridentate Schiff bases, we succeeded in preparing a monomeric complex of formula $[Ni(L)(N_3)]$ (HL is shown below), in which azide acts as a terminal monodentate ligand. The present work constitutes

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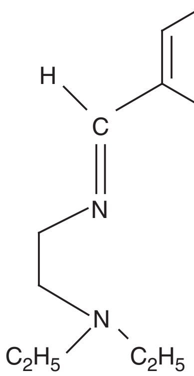
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500266024

part of a continuing study of metal-azido complexes containing tridentate Schiff base ligands of *N*-substituted ethylenediamine.



2. Experimental

2.1. *Materials and synthesis*

Nickel(II) nitrate hexahydrate (Aldrich) and sodium azide (Sigma) were used without further purification. All other chemicals were of AR grade and used as received.

Caution. Although our samples were stable during handling, metal azido complexes are potentially explosive; only a small amount of material should be prepared and it should be handled with care.

2.1.1. [Ni(L)(N_3)] (1). A methanolic solution (20 cm^3) of *N*,*N*-diethylethylenediamine (1 mmol, 0.106 g) was added to a methanolic solution (20 cm^3) of salicylaldehyde (1 mmol, 0.122 g) and the mixture stirred for 30 min. To this, nickel(II) nitrate hexahydrate (1 mmol, 0.290 g) dissolved in methanol was added with stirring for 10 min. Finally, 5 cm^3 of an aqueous solution of NaN_3 (2 mmol, 0.130 g) was added drop-wise to the mixture with continuous stirring. The solution was filtered and the reddish brown filtrate set aside. Red crystals formed within a few days were collected by filtration and dried in a desiccator (yield ca 60%). Anal. Calcd for $C_{13}H_{19}NiN_5O$ (%): C, 48.1; H, 5.8; N, 21.6. Found: C, 47.8; H, 5.8; N, 19.8. ^1H NMR (300 MHz, $CDCl_3$), chemical shifts (ppm): 1.8 (s, 6H), 2.2 (s, 2H), 2.5 (s, 2H), 2.9 (t, 2H), 3.4 (t, 2H), 6.5 (s, 1H), 7.1 (m, 4H).

2.2. *Physical measurements*

Elemental analyses (CHN) were performed using a Perkin-Elmer 240 instrument. IR spectra were recorded on a Nicolet Magna IR 750 Series II FTIR spectrophotometer. The instruments used for other measurements are reported earlier [7].

2.3. *X-ray crystallography*

A suitable crystal was selected for X-ray crystallographic analysis. Single-crystal diffraction data were collected on a Bruker–Nonius MACH3 diffractometer at room temperature using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

Table 1. Crystallographic data for the complex.

Empirical formula	$C_{13}H_{19}N_5NiO$
Formula weight	320.04
Temperature (K)	293
Space group	$P2_1/c$
a (Å)	6.688(1)
b (Å)	13.016(1)
c (Å)	16.962(2)
β (°)	97.96(1)
V (Å^3)	1462.2(3)
R_{int}	0.022
Z	4
F (000)	672
μ (mm^{-1})	1.33
Absorption correction	Empirical (ψ scans)
Maximum/minimum transmission	0.825, 0.556
ρ_{Calcd} (g cm^{-3})	1.454
$\theta_{min}/\theta_{max}$ (°)	2.4, 25.1
Crystal size (mm)	0.15 × 0.22 × 0.50
Reflections measured	2650
Unique reflections	2559
No. observed reflections [$I > 2\sigma(I)$]	1882
Refinement method	Full-matrix least-squares on F^2
R_1^a (observed reflections)	0.044
wR_2^b (observed reflections)	0.105
Goodness of fit, s (observed reflections)	1.06
R_1 (all reflections)	0.070
wR_2 (all reflections)	0.119
Largest difference peak and hole (e Å^3)	0.498, −0.400

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2]/\Sigma[w(F_o^2)]^{1/2}$.

Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods using the program SHELXS-97 [8] and refined on F^2 by least-squares method using anisotropic thermal parameters for non-hydrogen atoms [8]. Hydrogen atoms were placed at idealised positions and included in structure factor calculations by being made to 'ride' on the atoms to which they were bonded [8]. Neutral atom scattering factors were taken from Cromer and Weber [9] and anomalous dispersion effects were included in F_{Calcd} [10]. Crystallographic data are summarised in table 1.

3. Results and discussion

IR spectra of $Ni(L)(N_3)$ shows a strong band at 1640 cm^{-1} due to the azomethine group [12]. The υ_{as} band for the azido group appears at 2060 cm^{-1} and the δ band for at about 640 cm^{-1}. Similar characteristic bands for azides have been observed in a number of mononuclear and polynuclear azido-bridged complexes [5, 7]. In electronic spectra (methanol solution), a relatively weak band appears at around 610 nm, assigned as a d–d transition while a broad intense band centered around 365 nm is due to ligand to metal charge transfer. Magnetic measurements shows that the complex is diamagnetic.

3.1. *Description of the structure of [Ni(L)(N$_3$)] (1)*

An ORTEP [11] diagram of the complex showing the atom labelling scheme is shown in figure 1. The structure consists of a discrete molecule of [Ni(L)(N$_3$)]. The nickel ion occupies the central position of a regular square planar arrangement. Of its four coordination sites, three are occupied by the tridentate Schiff base through two nitrogen (amino and imino) atoms and the deprotonated phenoxy group. The remaining coordination site is satisfied by an azido ligand. Ni–N bond lengths are Ni–N1 = 1.840(3), Ni–N2 = 1.964(3), Ni–N3 = 1.899(3) Å, while Ni–O1 is 1.834(3) Å. Other selected bond lengths and angles are listed in table 2. Observed bond lengths and bond angles are in agreement with the other similar systems reported earlier [6]. The structure of the present complex, however, differs from those of copper(II) complexes containing terminal azido ligands [13]. The present complex acquires a square planar environment probably because of the two ethyl groups attached to the same N atom in the ethylenediamine backbone of the Schiff base ligand.

The coordinated azido anion is nearly linear [N3–N4–N5 = 175.45(4)°], but the (Ni–)N–N bond length [1.187(5) Å] is longer than the (Ni–N–)N–N

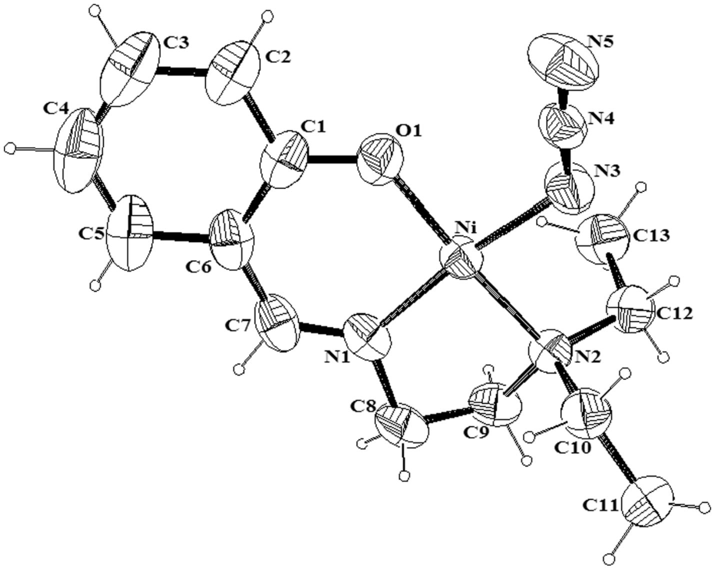


Figure 1. ORTEP diagram of [Ni(L)(N$_3$)] showing the atom labelling scheme with thermal ellipsoids drawn at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for [Ni(L)(N$_3$)].

Ni–O1	1.834(3)	N1–Ni–N2	86.54(1)
Ni–N1	1.840(3)	N1–Ni–N3	171.36(1)
Ni–N2	1.964(3)	O1–Ni–N1	95.5(1)
Ni–N3	1.899(3)	O1–Ni–N2	175.91(1)
N3–N4	1.187(5)	N2–Ni–N3	89.32(1)
N4–N5	1.153(5)	N3–N4–N5	175.45(4)
		O1–Ni–N3	89.13(1)
		Ni–N3–N4	122.68(3)

bond distance [1.153(5) Å]. This suggests that the covalency of the nickel(II)–azido bond is appreciable and the main contribution to the ground-state geometry of the coordinated azido is provided by the two canonical structures $–N{=}N^{+}{=}N^{-} \leftrightarrow –N^{-}–N^{+}{\equiv}N$.

The coordination of the phenoxy oxygen, O(1), and the imino nitrogen, N(1), to Ni(II) ion results in the formation of a planar six-membered ring. This, together with the phenyl ring, constitutes a ten-membered planar system. The structure shows that this planar moiety is stacked in the lattice with interplanar distances of 3.428 Å between pairs of chelate rings, 3.574 Å between pairs of phenyl rings, and 3.491 Å between pairs of rings of the two types.

Although there are no classical hydrogen bonds in the structure, two intermolecular and one intramolecular C–H···N contacts are observed. The conformations of the azide chain, about the N(3)–Ni coordination bond, and that of the ethyl side chain, about the N(2)–C(10) and the C(10)–C(11) single bonds, are locked by the formation of two C–H···N intermolecular contacts between translation-related moieties (table 3). An intramolecular C–H···N contact [C(12)–H(12B)···N(3)] further consolidates the interlocking of the terminal azide and ethyl groups of adjacent moieties.

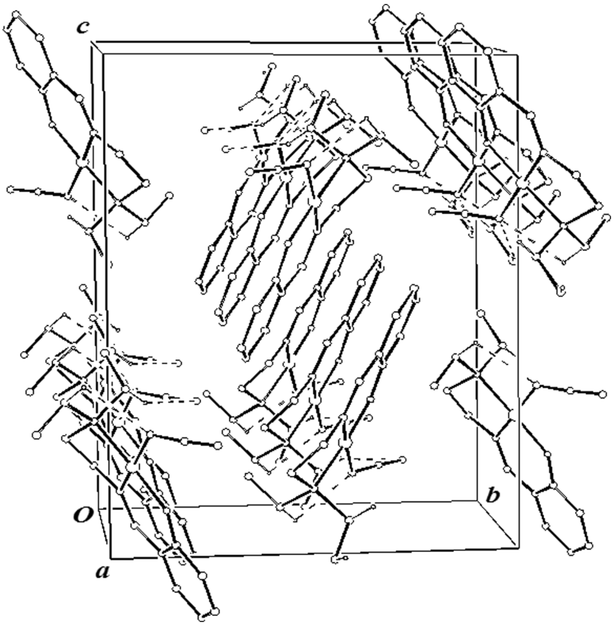


Figure 2. The unit cell contents of the complex showing interplanar stacking and C–H···N contacts (dashed lines).

Table 3. Details of C–H···N contacts in the crystal structure of the complex.

C–H···N	C–H (Å)	C···N (Å)	H···N (Å)	∠C–H···N (°)
C(10)–H(10A)···N(5)^{i}	0.97	3.408(6)	2.52	152
C(11)–H(11A)···N(3)^{i}	0.96	3.504(6)	2.60	157
C(12)–H(12B)···N(3)	0.97	2.894(6)	2.49	105

Symmetry equivalent (i) is $1-x$, y, z.

Supplementary data

Supplementary crystallographic data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) upon request, quoting deposition number CCDC 271688.

Acknowledgements

The work was financially supported by the University Grants Commission, New Delhi, by grant F.12-9/2002(SR-I) to SK. We are grateful to RSIC, CDRI, Lucknow for elemental analyses.

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