Inorganica Chimica Acta 462 (2017) 281–288

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Hydrogen bond directed 1D to 3D structures of square-planar Ni(II) complexes and their antimicrobial studies

Muhammet Kose [a,*], S. Eylul Duman [b], Vickie McKee [c], Ismail Akyol [d], Mukerrem Kurtoglu [a,*]

[a] Department of Chemistry, Kahramanmaras Sutcu Imam University, Kahramanmaras 46050, Turkey
[b] Necmettin Erbakan University, Seydisehir Vocational School, Konya, Turkey
[c] School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland
[d] Animal Science Genetics Unit, Faculty of Agriculture, Kahramanmaraş Sütçü İmam University, Kahramanmaraş 46050, Turkey

ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form 11 March 2017
Accepted 2 April 2017
Available online 6 April 2017

Keywords:
Dicyandiamide
Square-planar nickel(II) complexes
Hydrogen bonding
Crystal structure
Antimicrobial activity

ABSTRACT

A series of new mononuclear nickel(II) complexes derived from dicyandiamide (dcda) and $Ni(ClO_4)_2{\cdot}6H_2O$ in various alcohol solutions was synthesized and characterized. Nucleophilic addition of the alcohol to the nitrile (–C≡N) group of the dcda was observed in all complexes, yielding $[Ni(L\text{-}Me)_2](ClO_4)_2$ (**1**), $[Ni(L\text{-}Et)_2](ClO_4)_2$ (**2**), $[Ni(L\text{-}^nPr\text{-})_2](ClO_4)_2$ (**3**) and $[Ni(L\text{-}^nBu)_2](ClO_4)_2$ (**4**) in methanol, ethanol, *n*-propanol and *n*-butanol, respectively. The complexes were characterized by microanalysis (CHN), IR and mass spectroscopies. Crystal structures of the complexes (**2–4**) were determined by single crystal X-ray diffraction studies. In the structures of the synthesized complexes, the Ni(II) ion is in a square planar arrangement being coordinated to four nitrogen atoms of two *in situ* formed ligands. Hydrogen bonding directed packing of the structures were analysed. The structurally characterized complexes were then screened for their antibacterial activity against three different bacterial strains (*Lactococcus lactis*, *Streptococcus thermophilus* and *Escherichia coli*) using disk diffusion and spectrophotometric methods. The nickel(II) complexes displayed higher activity than dicyandiamide against the same microorganisms under identical experimental conditions.

1. Introduction

The design and construction of metal organic coordination compounds are of current interest in the fields of inorganic chemistry and crystal engineering. Metal complexes have found several applications in many areas of science, including catalysis [1], medicine [2], design of high value materials [3], analytical chemistry [4] and as model compounds with the structure and function of metalloproteins [5]. The metal oxidation state, the type and number of donor atoms, as well as their relative disposition within the ligand, are major factors determining the structure-activity relationships of the metal complexes [6]. Metal complexes with different oxidation states have a strong role in bioinorganic chemistry and redox enzyme systems [7,8], and may provide the basis of models for active sites of biological systems [9] or act as catalysts [10]. Nickel compounds also have useful applications such as ceramics [11], paints [12] and dyes [13], electroplating [14] and a mordant in the textile industry [15].

Dicyandiamide or cyanoguanidine contains an active nitrile group and has two tautomeric forms: $N{\equiv}C\text{–}N{=}C(NH_2)_2$ and $N{\equiv}C\text{–}NHC(=NH)NH_2$. It is used in the production of a wide variety of organic compounds including slow and continuous nitrogen release fertilizers [16], fire proofing agents [17], epoxy laminates for circuit boards [18], powder coatings [19] and adhesives [20], water treatment chemicals [21], dye fixing [22], leather and rubber chemicals [23], explosives [24], pharmaceuticals [25]. The dicyandiamide and its derivatives have been used as ligands for the preparation of coordination metal complexes. In the presence of transition metals, dicyandiamide usually undergoes nucleophilic addition reactions with water, alcohols and amines resulting in the guanylurea, 1-amidino-O-alkylureas, and biguanides, respectively [26–33]. Notably, no reaction occurs between alcohols and dicyandiamide in the absence of metal ions. In a typical reaction, alcohol addition to dicyandiamide in presence of Cu(II) with reflux results in high yields [34]. However, in the presence of Ni(II) the same reaction requires longer reaction times and a base and yields in these reactions are low [35].

Recently, we reported the synthesis, photophysical properties and biological activities of bidentate ligands and their metal complexes [36–39]. In continuation of our work, we described the

* Corresponding authors.
E-mail addresses: muhammetkose@ksu.edu.tr (M. Kose), kurtoglu01@gmail.com (M. Kurtoglu).

http://dx.doi.org/10.1016/j.ica.2017.04.005
0020-1693/

preparation and structural characterization of the square-planar nickel(II) complexes $[Ni(L\text{-}Me)_2](ClO_4)_2$ (**1**), $[Ni(L\text{-}Et)_2](ClO_4)_2$ (**2**), $[Ni(L\text{-}^nPr\text{-})_2](ClO_4)_2$ (**3**) and $[Ni(L\text{-}^nBu)_2](ClO_4)_2$ (**4**)] (Fig. 1). The antimicrobial activities of the Ni(II) chelates were also examined by disk diffusion and spectrophotometric methods.

2. Experimental

2.1. Materials

Dicyandiamide (dcda) was purchased from Aldrich Chemical Company and $Ni(ClO_4)_2{\cdot}6H_2O$ from Strem Chemical Company, USA. All other materials used in the present work were reagent grade quality provided from Merck or Aldrich and used as received.

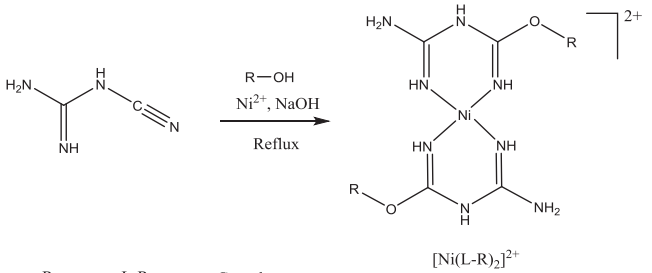
Caution: Salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities.

2.2. Physical measurements

Microanalytical (carbon, hydrogen and nitrogen) data were obtained with a model CE-440 elemental analyzer. Mass spectra were recorded on a Thermo Fisher Exactive + Triversa Nanomate mass spectrometer. The IR spectra were obtained (4000–400 cm^{-1}) using a Perkin Elmer spectrum 100 FTIR spectrophotometer. X-ray crystallographic data for the complexes were collected at 150(2) K on a Bruker Apex(II) CCD diffractometer using Mo-$K\alpha$ radiation (λ = 0.71073 Å) [40]. Data reduction was performed using Bruker SAINT [40]. SHELXS97 was used to solved and SHELXL2014/6 to refine the structure [41]. The structures were solved by direct methods and refined on F^2 using all the reflections [41]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon atoms were inserted at calculated positions using a riding model. Hydrogen atoms bonded to nitrogen atoms were located from difference maps and refined with temperature factors riding on the carrier atom. In the structure of $[Ni(L\text{-}Et)_2](ClO_4)_2$, the perchlorate anion is disordered and was modelled with 50% occupancy of two overlapping sites. Details of the crystal data and refinement are given Table 1. Hydrogen bond parameters for the complexes are given in the Supplementary material.

2.3. Synthesis of the complexes

The complexes were prepared by the reaction of two equivalents of dicyandiamide with one equivalent of $Ni(ClO_4)_2{\cdot}6H_2O$ in presence of a base (NaOH) in the corresponding alcohol [31]. A typical preparation is described in the Section 2.3.1.



R	L-R	Complexes
Me	L-Me	$[Ni(L\text{-}Me)_2](ClO_4)_2$ (**1**)
Et	L-Et	$[Ni(L\text{-}Et)_2](ClO_4)_2$ (**2**)
^{n}Pr	L-^{n}Pr	$[Ni(L\text{-}^nPr)_2](ClO_4)_2$ (**3**)
^{n}Bu	L-^{n}Bu	$[Ni(L\text{-}^nBu)_2](ClO_4)_2$ (**4**)

Fig. 1. General structure of Ni(II) complexes prepared in this study.

2.3.1. $[Ni(L\text{-}Me)_2](ClO_4)_2$ (**1**)

$Ni(ClO_4)_2{\cdot}6H_2O$ (2.18 g, 5.95 mmol) dissolved in 20 mL of methanol was added to dicyandiamide (1 g, 12 mmol) in methanol (15 mL). To this solution, NaOH (0.08 g, 2 mmol) dissolved in 10 mL of hot MeOH was added dropwise. The reaction mixture was refluxed for two days and then left to cool. The precipitated product was filtered off, washed several times with MeOH and diethyl ether and left to dry in air.

Colour: Orange; Yield: 1.035 g, 35%; M.p. = 282–283 °C (decomp.); Characterization: Anal. Calc. for $C_6H_{16}Cl_2N_8NiO_{10}$ (489.84 g/mol): C, 14.71; H, 3.29; N, 22.88. Found: C, 14.37; H, 3.05; N, 22.57%; IR(cm^{-1}): 3455 ν_{as}(N–H), 3366 ν_s(N–H), ν(N–H), 3248 ν(alkyl C–H), 1655 ν(C=N), 1243 ν(C–O–C), 1071 (ClO_4^-), 618 (ClO_4^-), 556 ν(Ni–N); ESI-MS [*m*/*z* (rel. intensity) assignment]: 289(100%) $\{[Ni(L\text{-}Me)_2]ClO_4\}^+$.

The same experimental procedure to form (**1**) was followed to obtain complexes (**2**–**4**) except using different alcohols [(**2**) ethanol, (**3**) *n*-propanol, (**4**) *n*-butanol].

2.3.2. $[Ni(L\text{-}Et)_2](ClO_4)_2$ (**2**)

Colour: Orange; Yield: 0.322 g, 10.5%; M.p. = 297–298 °C (decomp.); Characterization: Anal. Calc. for $C_8H_{20}Cl_2N_8NiO_{10}$ (517.89 g/mol): C, 18.55; H, 3.89; N, 21.64. Found: C, 18.41; H, 3.55; N, 21.54%; IR(cm^{-1}): 3446 ν_{as}(N–H), 3346 ν_s(N–H), 3242 ν(N–H), 2993 ν(alkyl C–H), 1655 ν(C=N), 1241 ν(C–O–C), 1054 (ClO_4^-), 620 (ClO_4^-), 553 ν(Ni–N); ESI-MS [*m*/*z* (rel. intensity) assignment]: 317(100%) $\{[Ni(L\text{-}Et)_2]ClO_4\}^+$.

2.3.3. $[Ni(L\text{-}^nPr)_2](ClO_4)_2$ (**3**)

Colour: Orange; Yield: 0.707 g, 21.75%; M.p. = 290–291 °C (decomp.); Characterization: Anal. Calc. For $C_{10}H_{24}Cl_2N_8NiO_{10}$ (545.95 g/mol): C, 22.00; H, 4.43; N, 20.52. Found: C, 22.31; H, 4.13; N, 20.38%; IR(cm^{-1}): 3456 ν_{as}(N–H), 3345 ν_s(N–H), 3243 ν(N–H), 2977 ν(alkyl C–H), 1655 ν(C=N), 1242 ν(C–O–C), 1064 (ClO_4^-), 619 (ClO_4^-), 556 ν(Ni–N); ESI-MS [*m*/*z* (rel. intensity) assignment]: 345(100%) $\{[Ni(L\text{-}^nPr)_2]ClO_4\}^+$.

2.3.4. $[Ni(L\text{-}^nBu)_2](ClO_4)_2$ (**4**)

Colour: Orange; Yield: 0.760 g, 22.2%; M.p. = 273–274 °C (decomp.); Characterization: Anal. Calcd. for $C_{12}H_{28}Cl_2N_8NiO_{10}$ (572.07 g/mol): C, 25.11; H, 4.92; N, 19.52. Found: C, 25.33; H, 5.14; N, 20.21%; IR(cm^{-1}): 3441 ν_{as}(N–H), 3343 ν_s(N–H), 3229 ν(N–H), 2941 ν(alkyl C–H), 1662 ν(C=N), 1244 ν(C–O–C), 1051 (ClO_4^-), 620 (ClO_4), 564 ν(Ni–N); ESI-MS [*m*/*z* (rel. intensity) assignment]: 373(100%) $\{[Ni(L\text{-}^nBu)_2]ClO_4\}^+$.

2.3.5. Bacterial strains and culture collection

References strains *Lactococcus lactis* subsp. Lactis strain IL1403 [42]. *Streptococcus thermophilus* (NCFB2993) and *Escherichia coli* strain EC1000 [43] were used to determine if the synthesized nickel(II) metal complexes affect bacterial growth. IL1403 strain was grown at 30 °C without aeration in 10 mL GM17 medium. *Streptococcus thermophilus* (NCFB2993) strain was grown in SM17 at 42 °C and *Escherichia coli* (EC1000) strain was grown in LB medium at 37 °C with aeration in 10 mL LB medium. The synthesized metal complexes were dissolved in DMSO in various (25, 50, 75, 150 and 250 mg/mL) concentration and added 10 mL growth media in different concentration. All bacterial growths were replicated three times and at the end of the 24th hour growths were measured at OD_{600} using spectrophotometer (Spectramax Plus 384, California, US).