NICKEL COMPLEXES OF N,N,N',N'-TETRAKIS-(2-BENZIMIDAZOLYLMETHYL)-1,2-DIAMINOETHANE (L) AND THE X-RAY CRYSTAL STRUCTURE OF {[NiL]²⁺[NiCl₂(H₂O)₃(C₂H₅OH)]}2Cl⁻(C₂H₅OH)

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Abstract—The preparation and properties of Ni(II) complexes of the title ligand (L) are described and the X-ray crystal structure of Ni₂LCl₄(H₂O)₃(C₂H₅OH)₂ is reported. The crystal structure shows that the two nickel ions are not bridged but exist as two distinct distorted octahedral species. Six coordination about one nickel ion is produced exclusively by L to give the cationic species [NiL]²⁺. The second nickel ion achieves six coordination through an interesting combination of ligands to produce the novel complex [NiCl₂(H₂O)₃(C₂H₅OH)]. Since the two remaining chloride ions are hydrogen bonded to two of the water molecules and the ethanol molecule of [NiCl₂(H₂O)₃(C₂H₅OH)] the entire complex can be considered to be formed by the cocrystallization of the large cation [NiL]²⁺ by the "large anion" {[NiCl₂(H₂O)₃(C₂H₅OH)]Cl₂}²⁻.

The ligand N,N,N',N'-tetrakis-(2-benzimidazolylmethyl)-1,2-diaminoethane (L) reacts with Cu (H₂O)₆(BF₄)₂ to give a six-coordinate [CuL]²⁺ ion of unusual geometry.¹ Reaction with an excess of Cu(NO₃)₂(H₂O)₃ has given a ligand- and nitrate-bridged dimer [Cu₂L(NO₃)₃]⁺,² whilst CuClO₄ gives the Cu(I) dimer [Cu₂L]²⁺.² L is also known to react with Mo(CO)₆ to give the ligandbridged dimer Mo₂(CO)₆L.³ We are particularly interested in dimeric nickel complexes, in which the metal atoms are within approximately 6 Å of each other, as potential models for our EXAFS studies of the enzyme urease.⁴ In view of this it was decided to investigate the coordination chemistry of L with a series of Ni(II) salts in the hope of generating suitable EXAFS models.

EXPERIMENTAL

L was synthesized as described previously and characterized using NMR and mass spectroscopy.⁵ NiL(ClO₄)₂·2H₂O, NiL(NO₃)₂, NiLCl₂·2H₂O, NiLBr₂·2(C₂H₅OH) and NiL(SCN)₂ were all prepared by the same general method, viz. the appropriate metal salt was dissolved in hot ethanol and this was added slowly to a hot ethanolic solution of ligand. The crystalline product which formed rapidly was filtered off, and dried *in vacuo*. A metal: ligand ratio of 2:1 was used for these preparations.

 $Ni_2LCl_4 \cdot 6H_2O$

 $NiCl_2 \cdot 6H_2O(0.59 \text{ g})$ was dissolved in the minimum volume of hot ethanol and then diluted with acetone (30 cm³). To this was added dropwise a

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solution of L (0.73 g) in acetone (30 cm^3) . A pale blue product formed which could not be recrystallized from acetone. This was filtered off and dried *in vacuo*.

 $Ni_2LCl_4(H_2O)_3(C_2H_5OH)_2$

To a stirred hot mixture of NiCl₂ \cdot 6H₂O (0.59 g) and nitromethane (30 cm³) was added sufficient ethanol to give a clear solution. To this was added dropwise a solution of L (0.73 g) in nitromethane (30 cm³). The resulting dark green solution was heated and stirred for a few minutes, when a pale blue product formed. On cooling the blue product redissolved, and on standing for 2 weeks the solution gave brown microcrystals in low yield. The crystals used in the X-ray study were obtained by successive filtrations of a crystallizing solution until large single crystals formed.

$Ni_2LBr_4 \cdot 2H_2O \cdot C_2H_5OH$

NiBr₂·3H₂O (0.45 g) was dissolved in the minimum volume of hot ethanol, and the solution diluted with 30 cm³ of acetone. To this was added dropwise a solution of L (0.47 g) in acetone (30 cm³). A purple product formed which turned bluegrey on filtering and vacuum drying at 70°C.

$Ni_2LBr_4 \cdot 3H_2O$

NiBr₂·3H₂O (0.45 g) was dissolved in the minimum volume of hot ethanol and then diluted with hot nitromethane (30 cm³). To this was added dropwise a hot solution of L (0.47 g) in nitromethane (30 cm³). A blue product formed which was filtered off and air dried, which caused a colour change to grey on the surface and green in the bulk of the material. The green product was separated and dried at 70° C *in vacuo*.

Ni₂L(SCN)₄

Ni(SCN)₂ was prepared from KSCN (0.97 g) and Ni(NO₃)₂·6H₂O (0.73 g) in ethanol. To an ethanolic solution of Ni(SCN)₂ was added 30 cm³ of nitromethane followed by L (0.73 g) in nitromethane (30 cm³). The grey product that quickly formed was filtered off and dried *in vacuo*.

The analytical results for the above complexes are given in Table 1.

The diffuse-reflectance spectra were recorded on a Beckmann DK2 spectrophotometer and are given in Table 2.

Magnetic measurements (Table 2) were carried out at room temperature on a Gouy balance of conventional design.

X-ray crystallography

The crystal used for the X-ray study was sealed in a thin-walled glass capillary. All crystallographic measurements were made at 293 ± 2 K using a CAD4 diffractometer operating in the $\omega-2\theta$ scan mode, with Ni-filtered Cu- K_{α} radiation ($\lambda =$ 1.54178 Å) as previously described.⁶ The structure was solved via the heavy-atom method and refined using full-matrix least-squares using two blocks, one for atoms in each ion, and with scattering factors taken from Ref. 7. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were inserted in idealized positions, allowed

Table 1.	a
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	Analytical data of the complexes						
	Found (%)			Calc. (%)			
Complex	С	Н	N	С	Н	N	
$NiL(ClO_4)_2 \cdot 2H_2O$	47.0	3.9	15.8	46.7	4.1	16.0	
$NiL(NO_3)_2 \cdot 2H_2O$	51.7	4.7	19.9	51.0	4.5	21.0	
$NiLCl_2 \cdot 2H_2O$	54.7	5.4	17.4	54.7	4.9	18.8	
NiLBr ₂ ·2EtOH	50.8	4.9	15.5	51.2	5.0	15.7	
$NiL(SCN)_2 \cdot 2H_2O$	43.4	3.9	14.5	43.1	4.7	14.8	
Ni ₂ LCl ₄ ·6H ₂ O	43.4	3.9	14.5	43.1	4.7	14.8	
$Ni_2LCl_4 \cdot 3H_2O \cdot 2EtOH$	46.2	4.9	14.6	46.3	5.1	14.2	
$Ni_2LBr_4 \cdot 2H_2O \cdot EtOH$	39.2	3.5	12.9	39.3	3.8	12.7	
Ni ₂ LBr ₄ ·3H ₂ O	38.6	3.3	12.9	38.1	3.6	13.1	
Ni ₂ L(SCN) ₄	48.7	3.9	20.5	49.1	3.5	21.1	

^a EtOH is C₂H₅OH.

	Spe	ectral pea		
Complex ^a	(cm^{-1})	ν ₂ (cm ⁻¹)	ν ₃ (cm ⁻¹)	Magnetic moment
$NiL(ClO_4)_2 \cdot 2H_2O$	10,750	18,200	27,000	3.80
$NiL(NO_3)_2 \cdot 2H_2O$	10,650	17,900	28,600	3.62
NiLCl ₂ •2H ₂ O	10,200	17,900	27,800	2.98
NiLBr ₂ ·2EtOH	10,400	17,900	28,600	3.08
$NiL(SCN)_2 \cdot 2H_2O$	10,500	17,900	28,200	3.64
	Sp (n	ectral pea ot assigne	aks ed)	
$Ni_2LCl_4 \cdot 6H_2O$	8000, 11,000, 14,300 sh, 15,600			3.45
Ni ₂ LCl ₄ ·3H ₂ O·2EtOH	(9100–10,600) br, 18,200 sh, 21,750 sh, 24,400, 30,300			3.48
$Ni_2LBr_4 \cdot 2H_2O \cdot EtOH$	7250, 10,500, 13,300 sh, 14,300, 28,600			3.00
$Ni_2LBr_4 \cdot 3H_2O$	7700, 10,750, 13,500 sh, 14,500, 16,100 sh, 29,400			Insufficient sample
Ni ₂ L(SCN) ₄	Insufficie	nt sample	•	

Table 2. Diffuse-reflectance spectra and magnetic moments of the complexes

 a EtOH = C₂H₅OH.

 ${}^{b}v_{1} = {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F), v_{2} = {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F), v_{3} = {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ (in O_{h} -symmetry). sh = shoulder, br = broad.

to "ride" on the parent atom and assigned group isotropic thermal parameters. Computer programs used are listed in Ref. 6.

Crystal data. $[C_{34}H_{32}N_{10}Ni]^{2+}[C_2H_{12}O_4Cl_2Ni]$ $2Cl^- \cdot (C_2H_6O), M_r = 985.02, triclinic, a = 11.342(5),$ b = 11.611(1), c = 18.770(2) Å, $\alpha = 104.50(1),$ $\beta = 74.11(2), \gamma = 109.91(3)^\circ, V = 2201.2$ Å³, space group $P\overline{1}, Z = 2, D_c = 1.49$ g cm⁻³, μ (Cu = K_{α}) = 34.1 cm⁻¹, F(000) = 952.

Total unique data recorded, 4503 $(1.5^{\circ} \le \theta \le 50^{\circ})$, 2850 observed $[I > 1.5\sigma(I)]$.

Final R = 0.0615, $R_w = 0.0506$, weights $= 1/[\sigma^2 (F_o) + 0.00002F_o^2]$.

Tables of atomic positional and thermal parameters, bond lengths and angles, and F_o/F_c values have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic co-ordinates have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The structure of the title compound is shown in Fig. 1 where Cl(3) is hydrogen bonded to hydrogen atoms of water oxygens O(1) and O(2), and Cl(4) is hydrogen bonded to the hydrogen atoms of O(4)

(an ethanol molecule) and O(3) (a water molecule). Selected bond lengths and angles are given in Table 3. $[NiCl_2(H_2O)_3(C_2H_3OH)]$ exhibits facial geometry and the interesting feature of the molecule is the unusual combination of ligands utilized to achieve the distorted octahedral stereochemistry. [NiL]²⁺ is also distorted octahedral. The two distances Ni-N(13) (2.051 Å) and Ni-N(33) (2.058 Å) are very similar to the values found for other Ni(II) benzimidazole complexes.^{8,9} The other two Ni imino nitrogen distances, Ni-N(23) (2.101 Å) and Ni-N(42) (2.147 Å), are somewhat longer and presumably a consequence of the geometrical requirements of the ligand. The various bond angles centred at Ni range from 78.3 to 122.6° for cis groups and from 157.9 to 176.3° for trans groups. The most marked deviation from ideal geometry is the N(42)—Ni(1)—N(23) angle of 122.6° , the largest angle less than this being 96.8° for the cis N(13)-Ni(1)-N(2).

The complexes of stoichiometry NiLX₂ (X⁻ is ClO_4^- , NO_3^- , Cl^- , Br^- or SCN^-) have electronic spectral and magnetic properties which are consistent with the assignment of a structure similar to that of the cation in the title complex together with the appropriate anion, i.e. NiL²⁺2X⁻. The elec-



Fig. 1.

tronic spectra of the title complex can be interpreted as the superposition of the spectra due to the two species $[NiL]^{2+}$ and $[NiCl_2(H_2O)_3(C_2H_5OH)]$.

It could be argued that the electronic spectra of $Ni_2LCl_4 \cdot 6H_2O$ and the two forms of Ni_2LBr_4 contain features attributable to Ni(II) ions in octa-

hedral and tetrahedral environments. This would lead to the assignment of the structure $NiX_4^2 - NiL^{2+}$ to these complexes (X⁻ is Cl⁻, Br⁻ or SCN⁻) but their spectra do not show the relatively high intensity absorption bands associated with tetrahedrally coordinated Ni(II) complexes. In view of this,

Table 3. Selected bond lengths (Å) and angles (°)

Ni(1)—N(1)	2.186(9)	Ni(1)—N(2)	2.179(12)
Ni(1)—N(13)	2.051(9)	Ni(1)N(23)	2.101(12)
Ni(1)—N(33)	2.058(9)	Ni(1)—N(42)	2.147(10)
Ni(2)—Cl(1)	2.369(5)	Ni(2)Cl(2)	2.410(6)
Ni(2)O(1)	2.120(8)	Ni(2)—O(2)	2.090(12)
Ni(2)—O(3)	2.068(8)	Ni(2)—O(4)	2.085(8)
N(2)—Ni(1)—N(1)	81.8(4)	N(13)Ni(1)N(1)	81.3(4)
N(13)Ni(1)N(2)	96.8(4)	N(23) - Ni(1) - N(1)	78.3(4)
N(23) - Ni(1) - N(2)	157.9(3)	N(23) - Ni(1) - N(13)	89.5(4)
N(33)—Ni(1)—N(1)	95.5(4)	N(33)Ni(1)N(2)	80.8(5)
N(33) - Ni(1) - N(13)	176.3(3)	N(33) - Ni(1) - N(23)	91.7(5)
N(42)—Ni(1)—N(1)	158.2(4)	N(42) - Ni(1) - N(2)	78.4(4)
N(42)—Ni(1)—N(13)	92.2(4)	N(42) - Ni(1) - N(23)	122.6(4)
N(42)Ni(1)N(33)	90.1(4)		
Cl(1)-Ni(2)-Cl(2)	90.9(1)	Cl(1)Ni(2)O(1)	95.7(3)
Cl(2)—Ni(2)—O(1)	89.9(4)	Cl(1)— $Ni(2)$ — $O(2)$	87.8(3)
Cl(2)—Ni(2)—O(2)	175.4(2)	O(2)—Ni(2)—O(1)	85.9(4)
Cl(1)—Ni(2)—O(3)	172.9(3)	Cl(2)—Ni(2)—O(3)	95.4(4)
O(1)—Ni(2)—O(3)	87.6(4)	O(2)Ni(2)O(3)	86.2(4)
Cl(1)—Ni(2)—O(4)	92.1(3)	Cl(2)Ni(2)O(4)	87.9(4)
O(1)Ni(2)O(4)	171.9(3)	O(2)—Ni(2)—O(4)	96.9(4)
O(3)—Ni(2)—O(4)	84.8(4)		

assignment of a structure to these complexes will not be attempted. However, because of the possibility that some of these complexes might be of the structural type suitable for our EXAFS studies we are currently trying to grow crystals of them suitable for an X-ray crystallographic investigation.

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