The Co-ordination Chemistry of Divalent Cobalt, Nickel, and Copper. Part 10.† Characterisation and Stability Constants of Nickel(II) Species isolated from a Mixed-ligand Solution: Crystal Structure ‡ of Tris(1,2-diaminoethane)nickel(II) Bis(pyridine-2,6-dicarboxylato)-nickelate(II) Tetrahydrate

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The complexes, Ni(pydca)(en)·2H$_2$O (1), Ni(pydca)(en)$_3$·2H$_2$O (2), and Ni(pydca)(en)$_{1.5}$·2H$_2$O (3) were isolated from solutions of nickel(II), pydca, and en (pydca = pyridine-2,6-dicarboxylate, en = 1,2-diaminoethane). Spectral and magnetic data indicate that species (1) and (2) are octahedral and can be formulated as [Ni(pydca)(en)(H$_2$O)]·H$_2$O and [Ni(en)$_3$][pydca]·2H$_2$O, respectively. The structure of (3) was shown by Patterson and Fourier methods to be in accordance with the formula [Ni(en)$_3$][Ni(pydca)$_2$]·4H$_2$O, with a = 9.395(5), b = 10.924(5), c = 15.662(8) Å, α = 70.95(2), β = 101.36(2), γ = 104.91(2)°, Z = 2, triclinic, and space group $P\bar{1}$. Heating (1) gave a compound with the empirical formula Ni(pydca)(en). Infrared and magnetic data indicate that this species is monomeric and five-co-ordinate. A compound with the same empirical formula, Ni(pydca)(en), was obtained by heating (3), but spectral data and a magnetic moment of 3.40 B.M. for this product suggest the formula [Ni(en)$_2$][Ni(pydca)$_2$], containing [Ni(en)$_2$]$^{2+}$ with C_s symmetry. A plot of complex-ion concentrations as a function of Ni : en ratio in solution was derived from measured stability constants and was used to explain the stepwise isolation of species (1), (3), and (2).

This study deals with the complexes isolated from a solution containing nickel(II), pyridine-2,6-dicarboxylate (pydca), and 1,2-diaminoethane (en). It represents part of a long-term investigation of the stabilization of low-symmetry complexes (with special emphasis on five-co-ordinate species) by means of neutral donor ligands.[1-3]

The varied nature of the mixed-ligand complexes isolated herein prompted us to determine the stability constants for their formation and hence their distribution in solution.

It was possible to isolate three compounds from solutions containing [Ni(pydca)] and varying amounts of en, *viz.* Ni(pydca)(en)·2H$_2$O, Ni(pydca)(en)$_{1.5}$·2H$_2$O, and Ni(pydca)(en)$_3$·2H$_2$O. Careful heating of Ni(pydca)(en)·2H$_2$O, and of Ni(pydca)(en)$_{1.5}$·2H$_2$O produced complexes with the same empirical formula, Ni(pydca)(en), but with different types of metal co-ordination. All of these compounds were subjected to the usual analytical, spectral, and magnetic techniques to determine the metal co-ordination and to explain the unusual phenomena encountered upon heating. The nature of the compound Ni(pydca)(en)$_{1.5}$·2H$_2$O could not be established unambiguously by these methods and it was therefore decided to carry out a single-crystal *X*-ray analysis. Further motivation for complete structural determination was provided by the fact that this species was the starting material for the preparation of a Ni(pydca)(en) complex with unusual co-ordination.

Experimental

Preparations.—The starting material for the complexes was [Ni(pydca)]·3.5H$_2$O. This was prepared by dissolving pure sodium carbonate (42.0 g, 0.396 mol) in boiling water (1 dm^3) and adding, with constant stirring, pyridine-2,6-dicarboxylic acid (66.85 g) in small quantities. This was added dropwise to a solution of NiCl$_2$·6H$_2$O (94.8 g) in hot water (250 cm^3) and the resultant mixture slowly cooled to ±4 °C. Fine green crystals of [Ni(pydca)]·4H$_2$O were formed (yield 66%). A half water molecule was lost upon standing, producing [Ni(pydca)]·3.5H$_2$O.

Solid [Ni(pydca)]·3.5H$_2$O (2.86 g, 10 mmol) was dissolved in water (40 cm^3) containing en (0.68 g, 11.3 mmol). The solution was heated and filtered and absolute ethanol (35 cm^3) added to the filtrate. The solution was then reduced to 25 cm^3 by boiling, further hot absolute ethanol (50 cm^3) added, and then slowly cooled to −15 °C. Grass-like dark green crystals of Ni(pydca)(en)·2H$_2$O were formed (yield 30%). Anhydrous Ni(pydca)(en) was produced by heating Ni(pydca)(en)·2H$_2$O to 150 °C.

[Ni(pydca)]·3.5H$_2$O (6 g) was dissolved in a hot solution of en (1.7 g) in water (25 cm^3). Boiling absolute ethanol (150 cm^3) was added and the solution was slowly cooled to ±4 °C. Large dark purple crystals of Ni(pydca)(en)$_{1.5}$·2H$_2$O were formed (yield 60%).

[Ni(pydca)]·3.5H$_2$O (3 g) was dissolved in a solution of water (30 cm^3) and en (10 cm^3). After addition of boiling absolute ethanol (100 cm^3) and slow cooling to −15 °C, pink crystals of Ni(pydca)(en)$_3$·2H$_2$O were formed (yield 40%).

The complex [Ni(Hpydca)$_2$]·3H$_2$O was prepared by dissolving NiCl$_2$·6H$_2$O (5 g) in 95% ethanol (50 cm^3) and adding it dropwise to pyridine-2,6-dicarboxylic acid (8 g) in 95% ethanol (150 cm^3).

All reagents used were at least of reagent grade purity and, where necessary, were purified by standard techniques. The analytical data are given in Table 1.

Crystal Structure Determination of [Ni(en)$_3$][Ni(pydca)$_2$]·4H$_2$O.—*Crystal data.* (C$_6$H$_{24}$N$_6$Ni)$^{2+}$(C$_{14}$H$_6$N$_2$NiO$_8$)$^{2-}$·4H$_2$O,

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† Part 9 is ref. 3.

‡ *Supplementary data available* (No. SUP 23825, 58 pp.): structure factors, thermal parameters, H-atom co-ordinates, full bond distances and angles, full mean-plane data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical data for compounds prepared as described in the Experimental section and by thermogravimetric techniques

	Analysis * (%)				
Complex	Ni	en	C	H	N
$[Ni(pydca)(en)(H_2O)]\cdot H_2O$	18.1 (18.3)	18.5 (18.8)	33.8 (33.8)	4.6 (4.7)	13.1 (13.1)
$[Ni(pydca)(en)]$	20.3 (20.7)	20.9 (21.2)	37.8 (38.1)	4.1 (3.9)	15.1 (14.8)
$[Ni(en)_3][Ni(pydca)_2]\cdot 4H_2O$	16.9 (16.8)	26.1 (25.8)	34.9 (34.3)	5.5 (5.5)	16.4 (16.0)
$[Ni(en)_3][Ni(pydca)_2]$	18.7 (18.7)	28.7 (28.7)	37.8 (38.3)	5.1 (4.8)	17.5 (17.9)
$[Ni(en)_3][pydca]\cdot 2H_2O$	13.3 (13.3)	41.1 (41.0)	35.3 (35.5)	7.1 (7.1)	22.6 (22.3)
$[Ni(en)_2][Ni(pydca)_2]$	20.4 (20.7)	20.6 (21.2)	38.2 (38.1)	4.0 (3.9)	14.6 (14.8)
$[Ni(en)_3][pydca]$	14.2 (14.5)	45.0 (44.6)	38.4 (38.6)	6.8 (6.7)	24.5 (24.3)
$[Ni(Hpydca)_2]\cdot 3H_2O$	12.8 (13.2)	—	37.9 (37.8)	3.2 (3.2)	6.4 (6.3)

* Calculated values are given in parentheses.

$M = 700.1$, triclinic, space group $P\bar{1}$, $a = 9.395(5)$, $b = 10.924(5)$, $c = 15.662(8)$ Å, $\alpha = 70.95(2)$, $\beta = 101.36(2)$, $\gamma = 104.91(2)°$, $U = 1\,456.9$ Å^3, $D_m = 1.60$, $Z = 2$, $D_c = 1.60$ g cm^{-3}, $F(000) = 732$, $\mu(\text{Mo-}K_\alpha) = 12.9$ cm^{-1}, $\lambda = 0.7107$ Å.

Preliminary cell dimensions were obtained from Weissenberg and precession photographs (Cu-K_α radiation). They were refined by a least-squares fit of the angular settings of 25 high-order reflections measured on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. Intensity data were collected by the ω—2θ scan technique up to $\theta_{max.} = 23°$. Of the accessible 3 826 reflections, 1 667 had $I > 2\sigma(I)$ and were used in the final refinement. Lorentz-polarization corrections were applied, but no corrections were made for absorption in view of the shape and size of the crystal used (a parallelepiped, 0.16 × 0.16 × 0.20 mm).

A three-dimensional Patterson map indicated a centrosymmetric arrangement of the Ni atoms. The structure was developed by conventional Fourier techniques and refined successfully in space group $P\bar{1}$ by full-matrix least squares. Anisotropic thermal parameters were assigned to all atoms except those of the pyridine rings and the carbon atoms of the 1,2-diaminoethane ligands. Anisotropic refinement of the latter atoms did not improve the model significantly and resulted in matrix singularities for four atoms; the refinement scheme adopted was also dictated by the relatively small number of observations. The positions of the hydrogen atoms of the cation and anion were calculated geometrically and were included in a riding model with N–H and C–H = 1.08 Å. They were assigned common isotropic thermal parameters in five groups (two phenyl, three methylene) which refined to values in the range 0.06—0.10 Å^2. As it was not possible to locate the hydrogen atoms of the water molecules from difference maps, they were omitted from the calculations. Refinement converged at $R = 0.084$, $R' = 0.062$ with $w = 1/\sigma^2$. The average shift to estimated standard deviation ratio was 0.07 (max. 0.3) and the final difference map contained no peaks of height >0.6 e Å^{-3}. All calculations were performed with SHELX 76 [4] and XANADU programs. Figures were prepared with the CRISTEP system.[5]

The final atomic co-ordinates are given in Table 2, selected bond length, bond angle, and torsion angle data are given in Table 3.

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[Ni(en)_3][Ni(pydca)_2]\cdot 4H_2O$

Atom	*x*	*y*	*z*
Ni(1)	4 853(3)	4 060(2)	2 779(2)
O(11)	3 133(11)	2 748(11)	3 582(7)
O(21)	7 002(12)	5 230(11)	2 537(8)
O(31)	2 724(15)	1 875(15)	5 060(9)
O(41)	9 158(12)	6 053(11)	3 263(8)
N(11)	5 799(14)	3 998(13)	4 022(9)
C(21)	5 022(18)	3 351(16)	4 730(11)
C(31)	5 623(18)	3 408(16)	5 606(11)
C(41)	7 018(18)	4 183(16)	5 718(12)
C(51)	7 854(19)	4 851(16)	4 975(11)
C(61)	7 179(17)	4 720(15)	4 126(11)
C(71)	3 478(21)	2 563(18)	4 437(14)
C(81)	7 863(20)	5 412(17)	3 239(12)
O(12)	3 904(12)	5 718(11)	2 442(8)
O(22)	5 397(12)	2 406(10)	2 551(8)
O(32)	2 738(13)	7 091(12)	1 239(9)
O(42)	5 362(14)	1 555(12)	1 444(8)
N(12)	3 992(13)	4 201(13)	1 519(8)
C(22)	3 308(19)	5 198(17)	1 079(12)
C(32)	2 743(19)	5 293(17)	169(12)
C(42)	2 914(18)	4 471(17)	−275(12)
C(52)	3 634(18)	3 485(18)	198(12)
C(62)	4 171(17)	3 330(16)	1 113(11)
C(72)	3 305(20)	6 105(19)	1 645(13)
C(82)	5 046(19)	2 332(18)	1 760(12)
Ni(2)	9 274(3)	235(2)	2 714(2)
N(1)	9 639(15)	1 442(14)	3 608(10)
N(2)	9 066(16)	2 073(13)	1 711(9)
N(3)	6 997(13)	−429(13)	2 884(9)
N(4)	8 619(16)	−755(15)	1 692(9)
N(5)	11 603(14)	552(13)	2 612(9)
N(6)	9 791(15)	−1 422(13)	3 793(9)
C(1)	9 299(21)	2 764(19)	3 068(13)
C(2)	9 727(21)	3 099(20)	2 156(13)
C(3)	6 382(20)	−1 447(19)	2 433(13)
C(4)	7 012(21)	−1 118(19)	1 572(13)
C(5)	12 134(20)	−617(19)	3 203(12)
C(6)	11 394(19)	−1 168(18)	4 050(12)
$O_w(1)$	36(14)	3 031(13)	−1 520(9)
$O_w(2)$	537(13)	1 369(13)	313(8)
$O_w(3)$	2 783(15)	−95(13)	848(10)
$O_w(4)$	6 004(20)	764(17)	4 308(11)

Analysis and Characterisation.—Nickel(II) was analysed by potentiometric ethylenediaminetetra-acetic acid titration using a mercury drop electrode [6] after digesting in a 1 : 4 perchloric acid–nitric acid mixture (4 cm^3) for 15 h to remove pyridine-2,6-dicarboxylate. The 1,2-diaminoethane was analysed potentiometrically with a standard hydrochloric acid solution using a Metrohm E536 potentiograph. The water was determined by Karl-Fisher titration using a Metrohm E633 dead stop titrator. Elemental C, H, and N analyses were performed with a Heraeus Rapid Analyser. Infrared spectra were recorded on a Beckman 4250 i.r. spectrophotometer. The i.r. spectrum of the very hygroscopic Ni(pydca)(en) was recorded in a cold room at −4 °C on a Perkin-Elmer 457 spectrophotometer. Solid reflectance electronic spectra were obtained using a Beckman DK2A spectrophotometer with a magnesium oxide sphere. Where meaningful, electronic

Table 3. Selected bond lengths (Å), bond angles (°), torsion angles (°), and possible N–H $\cdots$ O hydrogen bond distances with estimated standard deviations in parentheses for $[Ni(en)_3][Ni(pydca)_2]\cdot4H_2O$

(*a*) Bond lengths

Ni(1)–O(11)	2.16(1)	Ni(2)–N(1)	2.15(1)
Ni(1)–O(21)	2.12(1)	Ni(2)–N(2)	2.14(1)
Ni(1)–O(12)	2.09(1)	Ni(2)–N(3)	2.12(1)
Ni(1)–O(22)	2.15(1)	Ni(2)–N(4)	2.12(1)
Ni(1)–N(11)	1.96(1)	Ni(2)–N(5)	2.16(1)
Ni(1)–N(12)	1.95(1)	Ni(2)–N(6)	2.12(1)

(*b*) Bond angles

O(11)–Ni(1)–O(21)	156.5(4)	N(1)–Ni(2)–N(4)	169.6(6)
O(12)–Ni(1)–O(22)	155.8(4)	N(2)–Ni(2)–N(6)	171.1(5)
N(11)–Ni(1)–N(12)	177.0(6)	N(3)–Ni(2)–N(5)	170.1(5)
O(11)–Ni(1)–N(11)	78.2(5)	N(1)–Ni(2)–N(2)	81.6(5)
O(21)–Ni(1)–N(11)	78.6(5)	N(3)–Ni(2)–N(4)	82.2(5)
O(12)–Ni(1)–N(12)	78.3(5)	N(5)–Ni(2)–N(6)	81.0(5)
O(22)–Ni(1)–N(12)	77.6(5)	N(1)–Ni(2)–N(3)	92.2(5)
N(11)–Ni(1)–O(12)	100.9(5)	N(1)–Ni(2)–N(5)	93.6(5)
N(11)–Ni(1)–O(22)	103.3(5)	N(1)–Ni(2)–N(6)	92.6(6)
N(12)–Ni(1)–O(11)	104.7(5)	N(2)–Ni(2)–N(3)	96.2(5)
N(12)–Ni(1)–O(21)	98.6(5)	N(2)–Ni(2)–N(4)	90.2(6)
O(11)–Ni(1)–O(12)	94.5(4)	N(2)–Ni(2)–N(5)	92.6(5)
O(11)–Ni(1)–O(22)	90.8(4)	N(3)–Ni(2)–N(6)	90.7(5)
O(21)–Ni(1)–O(12)	93.0(4)	N(4)–Ni(2)–N(5)	93.2(6)
O(21)–Ni(1)–O(22)	91.4(4)	N(4)–Ni(2)–N(6)	96.2(6)

(*c*) Torsion angles

N(1)–C(1)–C(2)–N(2)	53.6
N(3)–C(3)–C(4)–N(4)	49.8
N(5)–C(5)–C(6)–N(6)	55.4

(*d*) Hydrogen bond lengths

N–H $\cdots$ O	N $\cdots$ O	Proton amine type *
N(1)–H(1A) $\cdots$ O(11^{i})	3.288	ob
N(1)–H(1A) $\cdots$ O(31^{i})	3.346	ob
N(2)–H(2A) $\cdots$ O(42)	3.343	ob
N(2)–H(2B) $\cdots$ O_w(2^{i})	3.183	lel
N(3)–H(3A) $\cdots$ O(42)	3.050	ob
N(3)–H(3B) $\cdots$ O(31^{ii})	3.081	lel
N(4)–H(4A) $\cdots$ O_w(1^{iii})	3.168	ob
N(4)–H(4B) $\cdots$ O_w(2^{i})	3.067	lel
N(5)–H(5A) $\cdots$ O(11^{i})	3.142	ob
N(6)–H(6A) $\cdots$ O(41^{iv})	3.017	ob
N(6)–H(6B) $\cdots$ O(31^{ii})	3.090	lel

O_w(1) $\cdots$ O_w(2)	2.874
O_w(2) $\cdots$ O_w(3)	2.806
O_w(4) $\cdots$ O_w(4^{ii})	2.945
O_w(1) $\cdots$ O(32^{vi})	2.690
O_w(1) $\cdots$ O(41^{v})	2.769
O_w(3) $\cdots$ O(32^{iv})	2.922
O_w(3) $\cdots$ O(42)	2.820
O_w(4) $\cdots$ O(22)	2.793

Roman numeral superscripts indicate the symmetry operations: i $1 + x, y, z$; ii $1 - x, -y, 1 - z$; iii $1 - x, -y, -z$; iv $x, -1 + y, z$; v $1 - x, 1 - y, -z$; vi $-x, 1 - y, -z$.

* These designations distinguish N-H vectors nearly parallel (lel) to the pseudo-C_3 axes of the cation from those which make an oblique angle (ob) with them.

spectra were resolved into Gaussian components by means of a non-linear least-squares technique.[7,8] Thermogravimetric curves were obtained using a Perkin-Elmer TGS2 balance and a System 4 Microprocessor Controller. Magnetic measurements were performed as previously described.[9]

Stability Constants.—Stability constants were determined by the competitive ion method using a Metrohm E109 pH electrode. All measurements were made in a constant temperature laboratory regulated to 25 °C. During pH measurements, the solution and electrode system were kept in a vessel thermostatted to 25.0 ± 0.1 °C. A constant ionic strength of 0.2 mol dm^{-3} was maintained by the addition of sodium perchlorate. All measurements were made in triplicate using a Metrohm E636 Titroprocessor which was calibrated with four primary buffers.[10] Calculations were performed with a modified version of the program Miniquad.[11]

Results and Discussion

The characterisation of the species $Ni(pydca)(en)\cdot2H_2O$ and $Ni(pydca)(en)_3\cdot2H_2O$ isolated from solution was relatively straightforward. Their spectral, thermogravimetric, and magnetic properties are summarised in Tables 4 and 5. Thermogravimetric analyses indicated that the two water molecules in $Ni(pydca)(en)\cdot2H_2O$ are bonded differently. The absorption band in the i.r. spectrum at 525 cm^{-1}, which disappeared upon heating this compound, was in the correct region for assignment as ν(Ni–O)[12] and therefore indicated that one of the water molecules was co-ordinated to nickel. The single ν_{asym}(COO) absorbance at 1 630 cm^{-1} indicated similar monodentate co-ordination through both carboxylate groups.[13] The absorption bands which were found in pyridine-2,6-dicarboxylic acid (H_2pydca) at 420 and 645 cm^{-1} were both split and moved to higher energy upon complexation, indicating pyridine co-ordination.[12] The solution (in ethanol–water mixture) and the solid reflectance spectra of $Ni(pydca)(en)\cdot2H_2O$ were similar. The absorption coefficients and positions of the bands were typical of nickel(II) in a distorted octahedral co-ordination with nitrogen- and oxygen-donor ligands. The high absorption coefficient for the band at 27 800 cm^{-1} could be ascribed to intensity stealing from the adjacent charge-transfer peak. The magnetic moment of 3.14 B.M. is typical of an octahedral nickel(II) compound. Hence $Ni(pydca)(en)\cdot2H_2O$ is an octahedral complex with nickel co-ordinated to two carboxylate oxygens, one pyridine nitrogen, two amine nitrogens and one water oxygen atom and can be formulated as $[Ni(pydca)(en)(H_2O)]\cdot H_2O$.

The electronic solid reflectance spectrum of $Ni(pydca)(en)_3\cdot2H_2O$, Figure 1(*b*), strongly indicated the presence of a $[Ni(en)_3]^{2+}$ chromophore.[14] The reason that the absorption band at 30 000 cm^{-1} could not be found was that the intense charge-transfer absorbance masked all *d–d* transitions in this region. The i.r. spectrum contained a double band at 518 and 485 cm^{-1} which is also characteristic of $[Ni(en)_3]^{2+}$.[12] The magnetic moment of 3.11 B.M. is also consistent with a $[Ni(en)_3]^{2+}$ moiety. This compound can therefore be correctly formulated as $[Ni(en)_3][pydca]\cdot2H_2O$.

A similar analysis of the data for $Ni(pydca)(en)_{1.5}\cdot2H_2O$ did not permit an unambiguous structural assignment. A reasonable assignment from this empirical formula appeared to be a combination of the complex cation $[Ni(en)_3]^{2+}$ and the complex anion $[Ni(pydca)_2]^{2-}$. However, if this were the case, then its solid reflectance electronic spectrum should have closely resembled the sum of the electronic spectra of two compounds containing these complex ions separately. The solid reflectance spectra of $[Ni(en)_3][pydca]\cdot2H_2O$ (containing the cation) and of $[Ni(Hpydca)_2]\cdot3H_2O$ (which is known to contain the anion),[15] as well as that of $Ni(pydca)(en)_{1.5}\cdot2H_2O$ are illustrated in Figure 1. It is clear that the sum of the spectra of the first two complexes does not yield the spectrum of $Ni(pydca)(en)_{1.5}\cdot2H_2O$. A subsequent *X*-ray analysis showed the species to be correctly formulated as $[Ni(en)_3][Ni(pydca)_2]\cdot4H_2O$. The non-hydrogen atoms and the atomic nomenclature of the asymmetric unit are illustrated in Figure 2. The struc-

Table 4. Magnetic moments and i.r. (cm^{-1}) and electronic spectral data

Compound	Carboxylate co-ordination		Pyridine nitrogen co-ordination		Nitrogen (en) co-ordination		
	ν_{asym}(COO)	ν_{sym}(COO)			ν(Ni–N)	$\mu_{eff.}$[a]/ B.M.	Electronic spectra (nm)[b]
H_2pydca	1 700s	1 460, 1 420	645m	420m	510 (sh)	—	—
[Ni(pydca)(en)(H_2O)]·H_2O	1 630br, s	1 375s	693, 682	445, 429	510m[d]	3.14	1 080 (12.7), 865 (8.8), 858 (6.1), 360 (67.5)[c]
[Ni(pydca)(en)]	1 630br, s	1 370s	690, 682	442, 423	515, 485	3.17	1 040 (br), 580, 380 (sh on c.t.)[e]
[Ni(en)$_3$][Ni(pydca)$_2$]·4H_2O	1 620br, s	1 730s	715, 705	—	518, 485	3.23	[f]
[Ni(en)$_3$][pydca]·2H_2O	1 630br, s	1 375s	715, 705	—	515w	3.11	[f]
[Ni(en)$_2$][Ni(pydca)$_2$]	1 625s	1 375s	690, 680	445, 425w		3.40	1 030, 400 (sh on c.t.)

[a] At 25 °C; B.M. = 0.927 × 10^{-23} A m^2. [b] ε/dm^3 mol^{-1} cm^{-1} given in parentheses. [c] In aqueous ethanol (90%). [d] Additional band at 525 cm^{-1} due to ν(Ni–O) of oxygen (from H_2O) co-ordinated to Ni. [e] c.t. = Charge transfer. [f] See Figure 1 for spectrum.

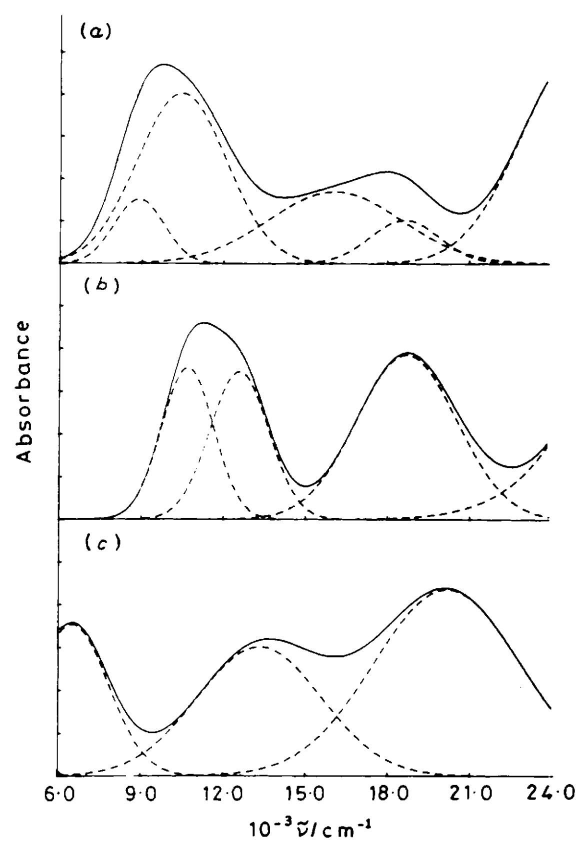

Figure 1. Solid reflectance spectra, resolved into Gaussian components, of (*a*) [Ni(en)$_3$][Ni(pydca)$_2$]·4H_2O, (*b*) [Ni(en)$_3$][pydca]·2H_2O, and (*c*) [Ni(Hpydca)$_2$]·3H_2O

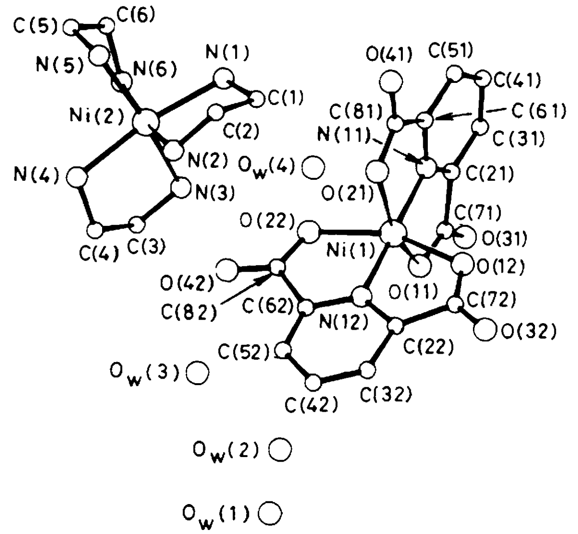

Figure 2. Molecular structure of [Ni(en)$_3$][Ni(pydca)$_2$]·4H_2O and atom numbering (hydrogen atoms omitted for clarity)

ture consists of discrete [Ni(pydca)$_2$]$^{2-}$ anions of approximately D_{2d} point symmetry in association with [Ni(en)$_3$]$^{2+}$ cations. In addition to anion–cation N–H ··· O hydrogen bonding, the water molecules serve as links between ions, stabilizing the structure by an extensive network of hydrogen bonds. The versatility of the pydca ligand is evident from its occurrence in metal complexes as the neutral acid, as a monoanionic or a dianionic species or a mixture of these,[16,17] and as a bridging ligand.[18] In this compound, both pydca ligands are tridentate and formally dianionic. The co-ordination geometry around Ni(1) is distorted octahedral with the pydca planes mutually perpendicular (dihedral angle 90.7°). Maximum deviations from the least-squares planes, including the twelve ligand atoms in each case, are 0.085 Å [atom O(31)] and 0.12 Å [atom O(42)]. The scatter in Ni–O bond lengths [range 2.09(1)—2.16(1) Å] is somewhat larger than would be expected for chemically identical bonds. In [Ni(Hpydca)$_2$]·3H_2O,[19] where it has been clearly established that each pydca ligand is monoanionic, the Ni–O(carboxylate) distances are 2.098(4) and 2.096(4) Å whereas the Ni–O(carbonyl) distances are 2.168(4) and 2.194(4) Å.

The centrosymmetric cell contains complex cations in both the $\Lambda\delta\delta$ and $\Lambda\lambda\lambda$ configurations.[20] Discussion is confined to the former configuration which is the one appearing in Figures 2 and 3 and for which atomic co-ordinates are listed. Bond lengths and angles in the cation are within the expected ranges. The factors influencing the ring conformations in [M(en)$_3$]$^{m+}$ have been discussed in detail.[21,22] From geometrical calculations with M = Cr (m = 3), it has been shown [22] that the volumes of the four unique isomers are not significantly different. This indicated, contrary to earlier suggestions, that the size of the counter ion should not have a bearing on which isomer prevails in the solid state. In particular, high-energy λ ring conformations are not necessarily favoured by the presence of large anions. The compound [Cr(en)$_3$][MoO(OH)-

Table 5. Summary of some pertinent data obtained from non-isothermal thermogravimetric curves

	Reaction	Temp. range (°C)	Experimental loss (%)	Calculated loss (%)
(*i*)	$[Ni(pydca)(en)(H_2O)]\cdot H_2O \longrightarrow [Ni(pydca)(en)(H_2O)] + H_2O$	50—110	5.6	5.6
(*ii*)	$[Ni(pydca)(en)(H_2O)] \longrightarrow [Ni(pydca)(en)] + H_2O$	110—150	5.7	6.0
(*iii*)	$[Ni(en)_3][Ni(pydca)_2]\cdot 4H_2O \longrightarrow [Ni(en)_3][Ni(pydca)_2]\cdot H_2O + 3H_2O$	40—120	7.4	7.7
(*iv*)	$[Ni(en)_3][Ni(pydca)_2]\cdot H_2O \longrightarrow [Ni(en)_3][Ni(pydca)_2] + H_2O$	130—220	3.0	2.8
(*v*)	$[Ni(en)_3][Ni(pydca)_2] \longrightarrow [Ni(en)_2][Ni(pydca)_2] + en$	220—310	9.5	9.6
(*vi*)	$[Ni(en)_2][Ni(pydca)_2] \longrightarrow$ indefinite products	310—350	20	—
(*vii*)	$[Ni(en)_3][pydca]\cdot 2H_2O \longrightarrow [Ni(en)_3][pydca] + 2H_2O$	70—125	8.3	8.2
(*viii*)	$[Ni(en)_3][pydca] \longrightarrow$ indefinite products	170—250	26	—

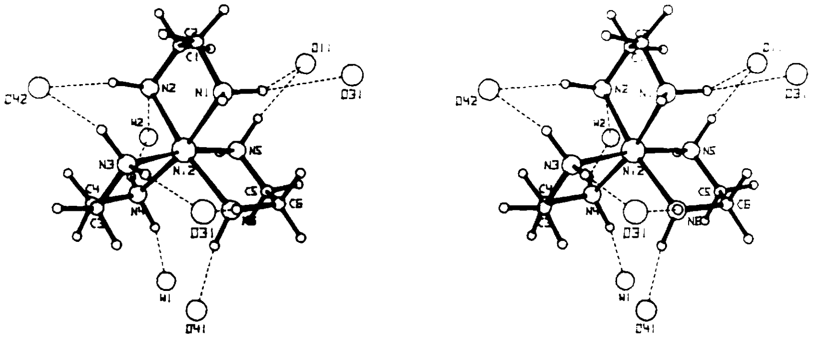

Figure 3. Stereoscopic view of the cation $\Lambda[Ni(en)_3\delta\delta\delta]^{2+}$ showing hydrogen bonding. The view direction is almost parallel to the pseudo-C_3 axis

$(CN)_4]\cdot H_2O$ was quoted[22] as an example in which a large complex anion is associated with a $\Lambda\delta\delta\delta$ cation. The title compound, containing the large $[Ni(pydca)_2]^{2-}$ species in the presence of a $\Lambda\delta\delta\delta$ cation provides further convincing evidence that anion size is not a factor which governs the cation configuration. Instead, the presence of a large number of potential Lewis-base acceptor sites (four hydrate oxygen atoms and the eight oxygen atoms of pydca) should favour a configuration which is most easily stabilized by hydrogen bonding. In a medium where the acceptor sites are close together, this configuration is $\Lambda\delta\delta\delta$.[22] Since the amine hydrogen-atom positions were calculated, hydrogen bonding has been inferred from appropriate N · · · O distances associated with favourable N–H · · · O angles. Distances up to a maximum of 3.35 Å for N · · · O have been included in Table 3, but the longer distances clearly represent rather weak interactions. Hydrogen bonding to the cation is shown in Figure 3. The situation resembles that observed in $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$,[23] and similar arguments[22] regarding the $\Lambda\delta\delta\delta$-stabilizing effects apply. Important stabilizing features are hydrogen bonds from two amine protons to the same oxygen acceptor atom. This occurs in four cases: two sets of ob proton pairs [on N(2), N(3) and on N(1), N(5)] are hydrogen bonded to single atoms [O(42) and $O(11^{I})$ respectively] while two sets of lel proton pairs [on N(2), N(4), and on N(3), N(6)] are likewise hydrogen bonded to single atoms [$O_w(2^{I})$ and $O(31^{II})$ respectively]. The designations lel and ob distinguish those N–H vectors nearly parallel to the pseudo-C_3 axes of the cation from those which make an oblique angle with these axes.[22] Since the hydrate hydrogen atoms were not located, the remaining hydrogen bonding has not been developed in detail, but the general features can be deduced from the distances listed in Table 3. Hydrate oxygen atoms $O_w(1)$, $O_w(2)$, and $O_w(3)$ are hydrogen bonded in a chain. The terminal atoms $O_w(1)$ and $O_w(3)$ form hydrogen bonds which link anions and cations while $O_w(2)$ stabilises the cation configuration as described above. Atom $O_w(4)$ is weakly hydrogen bonded to its centrosymmetric counterpart and links anions together *via* carboxylate oxygen atom O(22).

The results of the thermogravimetric analysis of this compound below 350 °C are summarised in Table 5. The C, H, and N analysis for the products of reactions (*iv*) and (*v*) are given in Table 1 and confirm their quoted empirical formulae. The loss of water in two discrete steps could not readily be explained from the *X*-ray structural data in view of the uncertainty in the H-atom positions. The proposed structural formula for the product of reaction (*v*), Table 5, is not unreasonable. The $[Ni(en)_2]^{2+}$ moiety has previously been isolated by precipitation in association with large anions.[24] It is therefore expected that the large $[Ni(pydca)_2]^{2-}$ anion can stabilize this species. Further support for this argument was the inability to obtain $[Ni(en)_2]^{2+}$ by heating $[Ni(en)_3][pydca]\cdot 2H_2O$, as indicated by reaction (*vii*), Table 5. The $[Ni(en)_2]^{2+}$ species which were previously isolated were shown to be diamagnetic square-planar complexes. The magnetic moment of $[Ni(en)_2][Ni(pydca)_2]$, Table 4, indicated that this $[Ni(en)_2]^{2+}$ species is paramagnetic. This can possibly be rationalised by considering the structural data for $[Ni(en)_3][Ni(pydca)_2]\cdot 4H_2O$. Atom N(4) of one en ligand is fairly strongly hydrogen bonded to hydrate oxygen atoms $O_w(1^{III})$ and $O_w(2^{I})$, Figure 3. Heating of the compound with subsequent loss of these water molecules would destabilize the cation, rendering the N(4)-containing en ligand relatively more labile. It is possible that this ligand is then lost upon further heating, the remaining hydrogen bonds (involving anion O atoms) maintaining the relative positions of the other two en ligands. This results in a $[Ni(en)_2]^{2+}$ moiety with C_s symmetry.

The i.r. spectra of $[Ni(pydca)(en)(H_2O)]\cdot H_2O$ and of the compound [Ni(pydca)(en)], produced by heating the former, exhibited identical $\nu_{sym}(COO)$ and $\nu_{asym}(COO)$ absorption bands, thus indicating identical carboxylate co-ordination in

Table 6. Stability constants of 1,2-diaminoethane species in solution at a constant ionic strength of 0.2 mol dm^{-3}

Reaction	$\log_{10}\beta$
$en + H^+ \rightleftharpoons Hen^+$	9.910(0.003)
$en + 2H^+ \rightleftharpoons H_2en^{2+}$	16.995(0.007)
$Ni^{2+} + en \rightleftharpoons [Ni(en)]^{2+}$	7.392(0.007)
$Ni^{2+} + 2en \rightleftharpoons [Ni(en)_2]^{2+}$	13.662(0.013)
$Ni^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+}$	18.002(0.040)
$pydca^{2-} + H^+ \rightleftharpoons Hpydca^-$	4.532(0.005)
$pydca^{2-} + 2H^+ \rightleftharpoons H_2pydca$	6.399(0.008)
$Ni^{2+} + pydca^{2-} \rightleftharpoons [Ni(pydca)]$	7.05(—)
$Ni^{2+} + 2pydca^{2-} \rightleftharpoons [Ni(pydca)_2]^{2-}$	13.72(—)
$Ni^{2+} + pydca^{2-} + en \rightleftharpoons [Ni(pydca)(en)]$	14.232(0.010)

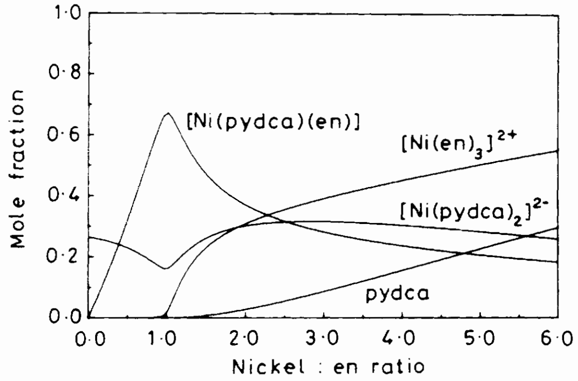

Figure 4. The variation in concentration of some selected species found in a 0.1 mol dm^{-3} [Ni(pydca)] solution upon addition of en using formation constants measured at an ionic strength of 0.2 mol dm^{-3}

these compounds. The ν_{asym}(COO) band found in the complex of empirical formula Cu(pydca)·2H_2O, where one carboxylate oxygen acts as a bridging atom, exhibits a strong extra absorption at 1 680 cm^{-1} which has been ascribed to dissimilar co-ordination.[13] Since such a band was absent from the above spectra, equivalent monodentate carboxylate co-ordination could be assumed. The solid reflectance electronic spectrum of [Ni(pydca)(en)] is very similar to that of [Ni(pydca)(en)(H_2O)]·H_2O. However, the spectra of distorted octahedral nickel(II) and five-co-ordinate nickel(II) frequently do not differ except for their molar absorptions. The absorption coefficients for [Ni(pydca)(en)] could not be determined since the complex was found to be insoluble in non-polar solvents. The magnetic moment is also consistent with five-co-ordinate nickel. This symmetry is therefore assigned to [Ni(pydca)(en)].

The stability constants for the formation of the various species found in a solution of Ni^{2+}, pydca, and en were determined, Table 6. Although the formation constant of [Ni(pydca)(en)] was the only one which had not been determined previously, those of most of the other species were redetermined since, for this system, any deviations in these constants could cause serious errors in the estimation of the constant for [Ni(pydca)(en)]. The stability constants for the formation of [Ni(pydca)] and $[Ni(pydca)_2]^{2-}$ were taken from literature [26] and corrections were made for variation in ionic strength.[27] A graph, illustrating the change in the concentrations of [Ni(pydca)(en)], $[Ni(en)_3]^{2+}$, $[Ni(pydca)_2]^{2-}$, and pydca for a 0.1 mol dm^{-3} [Ni(pydca)] solution upon increasing the en concentration, is shown in Figure 4. The fact that three different species were isolated from solution is easily explained. At a [Ni(pydca)] : en ratio of 1 : 1, the predominant species in solution is [Ni(pydca)(en)]. Hence, upon addition of ethanol, the solubility product of [Ni(pydca)(en)(H_2O)]·H_2O is exceeded. Similarly, at a [Ni(pydca)] : en ratio of between 2 : 1 and 3 : 1 both the $[Ni(en)_3]^{2+}$ and the $[Ni(pydca)_2]^{2-}$ concentrations are high, leading to the isolation of $[Ni(en)_3][Ni(pydca)_2]$·4H_2O. At [Ni(pydca)] : en ratios greater than 3 : 1, there is a steady increase in the $[Ni(en)_3]^{2+}$ concentration while the $[Ni(pydca)_2]^{2-}$ concentration decreases, causing a rapid increase in the pydca concentration, allowing the isolation of $[Ni(en)_3]$[pydca]·2H_2O.

Acknowledgements

The authors wish to acknowledge the financial assistance received from the South African Council for Scientific and Industrial Research, the South African Atomic Energy Board, and the University of Port Elizabeth. We also thank the C.S.I.R. for the services of the National *X*-ray Data Collection Facility in providing the diffractometer data.

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Received 22nd July 1983; *Paper* 3/1262