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The Coordination Chemistry of Divalent Cobalt, Nickel and Copper. Part II. The Characterisation of a Mixed Ligand Nickel(II) Species and Its Thermal Decomposition Products. The Crystal Structure of (Pyridine-2,6-dicarboxylato)(N,N,N′,N′-tetramethyl-1,2-diaminoethane)nickel(II) Dihydrate

JAN G. H. DU PREEZ, HANS E. ROHWER, BERNARDUS J. VAN BRECHT*

Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, South Africa

and MINO R. CAIRA

Crystallography Group, Chemistry Department, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, South Africa

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The magnetic and spectral properties of the complex $Ni(pydca)(tmen)\cdot 2H_2O$ *(1) and those of the thermally-derived species* $Ni(pydca)(tmen)\cdot H_2O$ *(2) and* $Ni(pydca)(tmen)$ *(3) have been studied (pydca = pyridine-2,6-dicarboxylate, tmen = N,N,N′,N′-tetramethyl-1,2-diaminoethane). Conflicting features in the electronic spectra prevented unambiguous stereochemical assignments. The presence of split* $\nu_s(COO)$ *and* $\nu_{as}(COO)$ *infrared absorption bands in the regions 1350–1400* cm^{-1} *and 1610–1680* cm^{-1} *respectively suggested dissimilar co-ordination of the carboxylate groups. The structure of (1) has been determined by the heavy-atom technique and refined by least-squares. Crystals are triclinic, space group* $P\bar{1}$*, with* $a = 10.806(5)$, $b = 8.626(4)$, $c = 9.825(5)$ Å, $\alpha = 114.32(2)$, $\beta = 91.52(2)$, $\gamma = 96.67(2)^\circ$, $d_{obs} = 1.50$ *(by flotation),* $d_{calc} = 1.51$ g cm^{-3} *and* $Z = 2$*. With* $N_{obs} = 2218$*, the final R factor was 0.047. Complex (1) is properly formulated as* $[Ni(pydca)(tmen)(H_2O)]\cdot H_2O$ *with Ni in a distorted octahedral environment, being bonded to two O atoms and the N atom of pydca, the two N atoms of tmen and one water molecule. The Ni–N(amine) distances differ significantly but structural parameters for the two carboxylate groups agree within experimental error. The anomalous spectral splitting appears to be common to analogous species containing fully-substituted diamines. Distorted octahedral and distorted square pyramidal symmetries are assigned to (2) and (3) respectively.*

Introduction

This study is part of a long-term investigation of the stabilization of low symmetry complexes, with special emphasis on pentacoordinate species [1–4].

The preparation and characterisation of the complex $Ni(pydca)(tmen)\cdot 2H_2O$ and its thermal decomposition products $Ni(pydca)(tmen)\cdot H_2O$ and $Ni(pydca)(tmen)$, (where pydca is pyridine-2,6-dicarboxylate and tmen is N,N,N′,N′-tetramethyl-1,2-diaminoethane) were further motivated by the possible use of substituted diamines in the concentration and separation of metal ions by solvent extraction methods investigated in these laboratories [5].

It was not possible to establish the nature of the coordination in the three complexes unambiguously from the usual magnetic, infrared and electronic spectral data and a number of interesting anomalies were found. It was therefore decided to carry out a single crystal X-ray analysis of $Ni(pydca)(tmen)\cdot 2H_2O$ to establish its structure unequivocally, and simultaneously to shed some light on the nature of the other complexes.

Experimental

Preparation

A solution of 0.205 mol $NiCl_2$ in 250 cm^3 water was added dropwise to 700 cm^3 of a hot solution containing 0.200 mol pyridine-2,6-dicarboxylic acid and 0.399 mol sodium hydroxide. The mixture was

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical and Magnetic Data.

Complex	%Ni		%tmen		%C		%H		%N		Magnetic Moment (B.M.)
	Exp.	Calc	Exp.	Calc	Exp.	Calc	Exp	Calc.	Exp	Calc.	
Ni(pydca)(tmen)•$2H_2O$	15.6	15.6	30.9	30.9	41.5	41.5	6.1	6.2	11.2	11.2	3.22
Ni(pydca)(tmen)•H_2O	16.4	16.4	32.5	32.5	43.6	43.6	5.9	5.9	11.7	11.7	3.17
Ni(pydca)(tmen)	17.2	17.3	34.2	34.2	45.3	45.9	5.8	5.6	12.3	12.4	3.21

slowly cooled to approximately 4 °C, and produced green crystals of Ni(pydca)•$4H_2O$. A mass of 6.0 g of this compound was dissolved in a boiling solution of 3 g N,N,N′,N′-tetramethyl-1,2-diaminoethane, 10 cm^3 water and 65 cm^3 methanol. Boiling ethyl acetate (150 cm^3) was added. On cooling slowly to 4 °C green, well-formed crystals of Ni(pydca)(tmen)•$2H_2O$ were obtained. Upon heating these to 100 °C, Ni(pydca)(tmen)•H_2O was formed, while heating to 150 °C produced Ni(pydca)(tmen).

Analytical and Characterisation

After 15 hours of digestion with 4 cm^3 of 1:4 perchloric acid/nitric acid mixture to destroy the organic ligands, the nickel(II) was analysed by potentiometric EDTA titration using a mercury drop electrode [6]. The N,N,N′,N′-tetramethyl-1,2-diaminoethane was analysed potentiometrically with a standard hydrochloric acid solution using a Metrohm E536 potentiograph. The water was determined by Karl Fischer titration using a Metrohm E633 dead-stop titrator. Elemental CHN analyses were performed with a Heraeus Rapid analyser.

Infrared spectra were determined on a Beckman 4250 infrared spectrophotometer. Solution electronic spectra were measured on a Perkin Elmer 330 spectrophotometer while solid reflectance spectra were measured on a Beckman DK2A spectrophotometer with a magnesium oxide integrating sphere. The electronic spectra were resolved into gaussian components by means of non-linear least-squares techniques [7, 8]. Thermogravimetric analyses were performed with a Perkin Elmer TG2 balance and a System 4 Microprocessor Controller. Magnetic measurements were performed as previously described [9].

Analytical and magnetic data are summarized in Table I.

Data Collection

Weissenberg and precession photographs taken with Cu-K_α radiation indicated that the crystals of the title compound are triclinic. For data collection an approximately equant specimen (0.12 X 0.12 X 0.16 mm) was prepared by grinding and etching a larger single crystal. Accurate cell dimensions were obtained by least-squares analysis of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The intensities of 2817 reflections in the range $6° < 2\theta < 50°$ were measured by the ω–2θ scan technique (scan width 0.8° θ, speed 0.027° θ s^{-1}), the background being measured on both sides of the peak for a total time equal to the peak scan time. Three reference reflections were monitored periodically during data collection. Their intensities showed no significant trends, thus indicating crystal stability. The final refinement was based on 2218 reflections with $I_o > 2\sigma(I_o)$, corrected for Lorentz and polarization effects. Absorption effects were negligibly small for the specimen used (μ(Mo-K_α) = 11.40 cm^{-1}).

Structure Determination and Refinement

The structure was solved by Patterson and Fourier methods and refined successfully in space group $P\bar{1}$. In the final cycles of refinement, all of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms of the organic ligands were geometrically placed in a riding model with C–H = 1.08 Å and with isotropic temperature factors fixed at 1.5 times those of their parent carbon atoms. The H atoms of the co-ordinated oxygen atom, O5, could not be located in difference electron-density maps. They were placed geometrically in positions dictated by hydrogen bonding and their parameters were not refined. The H atoms associated with atom O6 were clearly revealed in a difference synthesis but were also included with their parameters fixed. The refinement converged at R = 0.047, R_w = 0.045 with $w \propto 1/(\sigma^2(F_o) + gF_o^2)$; the factor g refined to 2.05×10^{-4}. The largest peak in the final difference map had a height of 0.77 $eÅ^{-3}$. All calculations were carried out with the SHELX-76 program system [10]. Figure 3 was prepared with the program CRISTEP [11]. Anisotropic thermal parameters, hydrogen atom positions and structure factor tables have been deposited. Fractional atomic co-ordinates are listed in Table II.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) for Non-hydrogen Atoms with Standard Deviations in Parentheses.

Atom	x	y	z
Ni	2558(0)	1530(1)	2421(1)
O1	667(2)	304(4)	1715(3)
O2	4550(2)	1663(4)	2481(3)
O3	–436(3)	–2332(4)	659(4)
O4	6043(3)	0(4)	1626(4)
O5	2632(2)	2097(4)	542(3)
O6	8486(3)	1838(4)	2829(4)
N1	2775(3)	–896(4)	1228(4)
N2	2342(3)	4100(5)	3737(4)
N3	2450(4)	1278(5)	4533(4)
C2	3933(4)	–1307(5)	1024(5)
C3	4118(4)	–2991(6)	204(5)
C4	3076(5)	–4233(6)	–350(6)
C5	1885(4)	–3789(6)	–131(5)
C6	1764(4)	–2083(5)	662(5)
C7	554(4)	–1320(6)	1033(5)
C8	4931(4)	250(6)	1767(5)
C9	2310(7)	4299(7)	5322(7)
C10	1860(8)	2737(9)	5455(8)
C21	3429(5)	5271(6)	3663(7)
C22	1209(5)	4575(6)	3235(7)
C31	1591(6)	–248(9)	4438(8)
C32	3630(6)	1172(11)	5185(8)

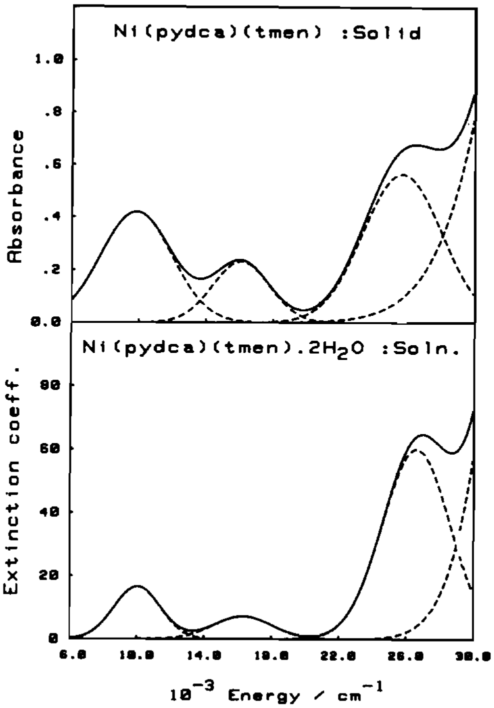

Fig. 1. The visible and near infrared solid reflectance spectrum of Ni(pydca)(tmen) and ethanol solution spectrum of [Ni(pydca)(tmen)(H_2O)]$\cdot H_2O$. The solid reflectance spectra of [Ni(pydca)(tmen)(H_2O)]$\cdot H_2O$, Ni(pydca)(tmen)(H_2O) and Ni(pydca)(tmen) are identical.

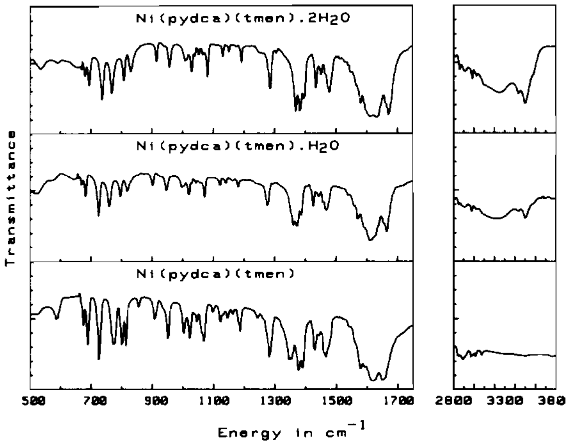

Fig. 2. The infrared spectra of [Ni(pydca)(tmen)(H_2O)]$\cdot$ H_2O, Ni(pydca)(tmen)(H_2O) and Ni(pydca)(tmen). The samples were prepared in KBr discs.

Results and Discussion

The spectral and magnetic data for Ni(pydca)(tmen)$\cdot 2H_2O$, Ni(pydca)(tmen)$\cdot H_2O$ and Ni(pydca)(tmen) are illustrated in Figs. 1, 2 and Table I. It was not possible to ascertain the environment of the nickel ions from these data and several anomalies arose. The magnetic moments of the three complexes were similar while their solid reflectance electronic spectra were identical. These results indicated similar nickel ion environments in each case, implying the absence of a water molecule from the coordination sphere. The latter conclusion could be rationalised if it was assumed that steric hindrance due to the large pydca ligand and the methyl groups of tmen prevented access to the sixth coordination site by water molecules. A similar explanation has been offered for the observed occurrence of pentacoordination in [Cu(tmen)(SO_4)(H_2O)$_2$]$\cdot H_2O$ [12]. On the other hand, the presence of bands with relatively low extinction coefficients in the solution electronic spectra (Fig. 1) indicated that a pentacoordinate environment was extremely unlikely, and that the nickel ions were probably in a distorted octahedral environment. Interesting features in the infrared spectra were the split ν_s(COO) and ν_{as}(COO) absorption bands in the regions 1350–1400 cm^{-1} and 1610–1680 cm^{-1} respectively (Fig. 2). This splitting could be interpreted as being due to dissimilar carboxylate groups in the pydca ligand.

The coordination of a carboxylate group may be monodentate, bidentate through two oxygen atoms [13], or bridging through one oxygen [14]. The latter coordination was found in Cu(pydca)$\cdot 2H_2O$

TABLE III. Selected Interatomic Distances (Å) and Angles (°) with Standard Deviations in Parentheses.

Ni–O1	2.144(3)	O1–Ni–O2	155.3(1)
Ni–O2	2.140(3)	N1–Ni–N2	178.6(2)
Ni–N1	1.979(3)	O5–Ni–N3	172.8(1)
Ni–N2	2.101(4)	N1–Ni–O1	77.6(1)
Ni–N3	2.178(4)	N1–Ni–O2	77.9(1)
Ni–O5	2.097(3)	O5–Ni–O1	90.5(1)
		O5–Ni–O2	87.7(1)
C7–O1	1.268(5)	N3–Ni–O1	91.0(1)
C8–O2	1.256(5)	N3–Ni–O2	93.8(1)
C7–O3	1.241(5)	N1–Ni–O5	92.4(1)
C8–O4	1.246(5)	N2–Ni–O1	102.9(1)
N1–C2	1.338(5)	N2–Ni–O2	101.7(1)
N1–C6	1.338(5)	N2–Ni–O5	89.0(1)
C2–C3	1.382(6)	N3–Ni–N1	94.8(1)
C3–C4	1.386(6)	N3–Ni–N2	83.8(2)
C4–C5	1.382(6)		
C5–C6	1.377(6)	O1–C7–C6	115.9(3)
C2–C8	1.521(6)	O2–C8–C2	116.4(3)
C6–C7	1.518(6)	O1–C7–O3	126.7(4)
N2–C9	1.496(7)	O2–C8–O4	126.3(4)
N3–C10	1.445(7)	C6–C7–O3	117.4(4)
C9–C10	1.438(9)	C2–C8–O4	117.2(4)
N2–C21	1.481(6)	C7–O1–Ni	114.3(2)
N2–C22	1.470(6)	C8–O2–Ni	114.3(3)
N3–C31	1.488(7)	Ni–N2–C9	106.9(3)
N3–C32	1.442(6)	Ni–N3–C10	103.3(3)

[14] and resulted in a split infrared ν_{as}(COO) absorbance similar to that described above. However, the infrared spectra of Ni(pydca)(tmen)·$2H_2O$ and Ni(pydca)(tmen)·H_2O contained absorption bands in the regions 3500 cm^{-1}, 3300–3200 cm^{-1} and 530 cm^{-1}, which are typical of water coordinated to a metal. This would be very unlikely if one of the carboxylate groups was bidentate or bridging. It was therefore decided to determine the structure of Ni(pydca)(tmen)·$2H_2O$ by single crystal X-ray analysis.

The asymmetric unit consists of the complex molecule Ni(pydca)(tmen)(H_2O) and an uncoordinated water molecule. This is illustrated in Fig. 3, which also shows the atomic numbering. Selected bond lengths and angles are listed in Table III; mean-planes, torsion angles, hydrogen bonds and selected contact distance data appear in Table IV. The Ni atom is in a distorted octahedral environment, being bonded to the pyridine nitrogen atom and two carboxylate oxygen atoms of pydca, the two nitrogen atoms of tmen, and an oxygen atom of a water molecule. The disposition of the organic ligands may be roughly described as mutually orthogonal with N1 *trans* to N2 and with N3 approximately *trans* to hydrate atom O5.

The Ni–O(carboxylate) distances are equal and fall within the range (2.09–2.16 Å) observed in

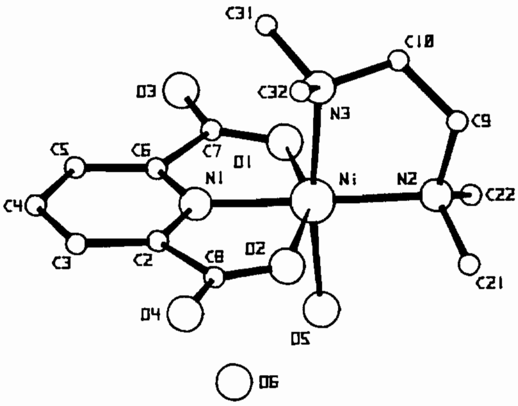

Fig. 3. The molecular configuration of [Ni(pydca)(tmen)(H_2O)]·H_2O showing atomic numbering. (Hydrogen atoms omitted).

$[Ni(en)_3][Ni(pydca)_2]\cdot 4H_2O$ [15] which contains four unique Ni–O bonds. Chemically equivalent bond lengths and angles in the pydca ligand are in very close agreement. The Ni–O5 distance (2.097(3) Å) compares very favourably with equivalent distances in $[Ni(en)(OH_2)_4](NO_3)_2$ [16].

There is a significant difference between the Ni–N(amine) distances. While the Ni–N2 distance (2.101(4) Å) is the same as that observed in Ni(tmen)$(O_2N)_2$ [17], (average 2.09(1) Å), the Ni–N3 distance is 2.178(4) Å. This lengthening may result from intramolecular non-bonded interactions between the methyl groups associated with N3, and atoms O1 and O2 of the pydca ligand. Non-bonded separations between these methyl C atoms and atoms O1 and O2 are similar and average 3.05 Å, whereas the equivalent distances involving the C atoms on N2, where interligand crowding is reduced, average 3.28 Å. These distances are all less than the accepted sum of the Van der Waals radii of 3.4 Å [18], and are included in Table IV. In addition, the Ni–N–C (methyl) angles are significantly larger at N3 than at N2 (average values 114.3 and 111.2° respectively, e.s.d.'s 0.3°). The angle between the normals to the pyridine plane and the plane defined by Ni–N2–N3 of tmen is 86.3°. Atoms C9 and C10 are not equally displaced from the Ni–N2–N3 plane, the torsion angle N2–C9–C10–N3 (49.3°) resulting primarily from the out-of-plane deviation of atom C10 (Table IV). Conformations of the N–C–C–N system, which have neither twofold nor mirror symmetry, are well known [19]. As a result of this asymmetry, atoms C31 and C32, although practically equidistant from atoms O1 and O2 respectively, are not symmetrically located with respect to the pydca ligand but are offset by rotation about the Ni–N3 bond. This asymmetry is reflected in the torsion angles O1–

TABLE IV. Least-squares Planes[a], Torsion Angles (°)[b], O–H···O Hydrogen-bond Data (A)[c] and Selected Shorter Contact Distances (A)[d].

	Plane no.	Deviations from plane (A)		r.m.s.d. (A)
(a)	1.	N1(0.005), C2(0.008), C3(–0.013) C4(0.008), C5(0.004), C6(–0.011)		0.009
	2.	C2(0.001), C8(–0.004), O2(0.002), O4(0.002)		0.003
	3.	C6(0.001), C7(–0.004), O1(0.002), O3(0.002)		0.002
	4.	Ni(0), N2(0), N3(0), C9*(0.074), C10* (–0.478)		0
(b)	N1–C6–C7–O1	4.7	O1–Ni–N3–C31	30.3
	N1–C2–C8–O2	1.6	O2–Ni–N3–C32	–3.7
	N2–C9–C10–N3	49.3		
(c)	O4···O6	2.863	O5···O3^{II}	2.688
	O4···H62	1.825	H52···O3^{II}	1.600
	O6···O1^{I}	2.859	O5···O4^{III}	2.730
	H61···O1^{I}	1.797	H51···O4^{III}	1.656
	I = 1 + x, y, z; II = –x, –y, –z; III = 1 – x, –y, –z; IV = –x, –1 – y, –z; V = 1 – x, 1 – y, 1 – z			
(d)	C21···O2	3.24	N3···O2	3.15
	C22···O1	3.33	N1···N3	3.06
	C31···O1	3.07	C31···C7	3.21
	C32···O2	3.03	C32···C8	3.49
	O5···C21	3.17	C5···O3^{IV}	3.35
	O5···C22	3.20	C2···O4^{III}	3.24
	N2···O1	3.32	C8···O4^{III}	3.38
	N2···O2	3.29	C8···C2^{III}	3.44
	N2···O5	2.94	C8···C8^{III}	3.32
	N3···O1	3.08	C9···O6^{V}	3.30

*Atoms not included in plane calculation.

Ni–N3–C31 (30.3°) and O2–Ni–N3–C32 (–3.7°). Consequently the pydca ligand is not rigorously planar, but slightly distorted by rotation of the planar carboxylate groups around the C6–C7 and C2–C8 bonds as evidenced by the torsion angles N1–C2–C8–O2 (1.6°) and N1–C6–C7–O1 (4.7°). There are however no significant differences in equivalent bond distances and angles in the carboxylate groups. Atom C8 of one of the carboxylate groups makes several close contacts with inversion-related carboxylate atoms (Table IV).

Both water molecules participate in O–H···O hydrogen bonding (Table IV). Complex molecules which are related by translation along the x-direction are linked by hydrogen bonding through hydrate atom O6 (in the relative position shown in Fig. 3). Each of the H atoms of the coordinated water molecule hydrogen bonds to different carbonyl O atoms (O3 and O4) of inversion-related molecules.

Splitting in the ν_{as}(COO) absorption, as observed in this complex, is usually ascribed to dissimilarity of the two carboxylate groups [14, 20]. The most frequently encountered difference lies in the extent to which the two groups are coordinated to the metal ion and this is usually reflected in the respective metal–oxygen bond lengths. As noted above, however, the Ni–O bond lengths are identical in this complex.

The different hydrogen bonding environments of the carboxylate groups were considered as a source of inequivalence of these groups. For atoms O1, O2, O3 and O4, the numbers of O···H–O hydrogen bonds to water molecules are (respectively) one, zero, one and two. However, the removal of the water molecules results only in a sharpening of the ν_{as}(COO) absorbance while the splitting remains. For the pydca system, there is the further possibility of electronic inequivalence of the carboxylate groups due to electron delocalisation from the pyridine ring. The extent of such delocalisation should be reflected in the degree of coplanarity of the various moieties involved, being a maximum when they are exactly coplanar. In this case, steric interactions appear to cause small differences in the orientations of the two carboxylate planes with respect to the pyridine ring plane. The sense of the N–C–C–O torsion angles quoted above results in an angle of 5.6° between the normals to the carboxylate mean planes. That these distortions are not responsible for the splitting is evidenced by the fact that the equivalent parameters in $[Ni(en)_3][Ni(pydca)_2]\cdot 4H_2O$ are similar (N–C–C–O 2–6.5°) and no spectral splitting is observed [15]. Furthermore, in the title complex, the C2–C8 and C6–C7 bond distances are equal (1.521(6), 1.518(6) Å), indicating equal extents of charge delocalisation for the two carboxylate groups.

The above evidence suggests that the splitting is in some way associated with the presence of a tetrasubstituted diamine in the complex. Further support for this suggestion is that for the species $Ni(pydca)(en)\cdot 2H_2O$ [15] and $Ni(pydca)(3en)\cdot 4H_2O$ [21] (en = 1,2-diaminoethane, 3en = 1,3-diaminopropane), where no steric interaction of the type described above is possible, a single symmetrical $\nu_{as}(COO)$ absorption band is observed, while in numerous analogous nickel complexes containing fully-substituted diamines, the $\nu_{as}(COO)$ is split [21]. It should be noted that although the observed splitting cannot be explained with certainty on the basis of one molecular structure determination, these results do emphasise the need for caution in assigning the band splitting in pydca and similar ligands to dissimilar carboxylate coordination [20, 22]. Other complexes containing fully-substituted diamines are being investigated in order to explain these spectral splitting effects.

The assignment of the electronic spectrum of $[Ni(pydca)(tmen)(H_2O)]\cdot H_2O$, resolved into gaussian components, can be done with some confidence since the complex is known to be octahedral:

$$^3T_{2g} \leftarrow {}^3A_{2g} \text{ at } 10\,040 \text{ cm}^{-1} \ (\epsilon = 16.6)$$

$$^3T_{1g} \leftarrow {}^3A_{2g} \text{ at } 16\,300 \text{ cm}^{-1} \ (\epsilon = 7.1)$$

$$^3T_{1g}(P) \leftarrow {}^3A_{2g} \text{ at } 26\,590 \text{ cm}^{-1} \ (\epsilon = 60)$$

where ϵ is the molar extinction coefficient.

The high extinction coefficient found for the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition can be ascribed to intensity-stealing from the charge transfer absorbance. Furthermore a very small absorption band, which could not be resolved by gaussian analysis of the spectrum, was detected in the region 13000 cm^{-1} and could possibly be ascribed to the spin-forbidden $^1E_g \leftarrow {}^3A_{2g}$ transition.

Since the $Ni(pydca)(tmen)(H_2O)$ complex was derived from the title complex $[Ni(pydca)(tmen)(H_2O)]\cdot H_2O$ by gentle heating, it is expected that their structures are similar. The sharp absorption at 3500 cm^{-1}, the broad band from 3300 cm^{-1} to 3200 cm^{-1} and the band at 525 cm^{-1} in the infrared spectrum, indicate coordinated water. Hence an octahedral coordination environment similar to that found in $[Ni(pydca)(tmen)(H_2O)]\cdot H_2O$ can be inferred for the monohydrate.

The stereochemistry of Ni(pydca)(tmen) must of necessity differ considerably from that of the complexes described above. Octahedral symmetry is possible *via* a bidentate or bridging carboxylate group. However, this should affect the infrared spectrum to a greater extent than was in fact observed.

The most likely stereochemistry for this complex is therefore pentacoordinate distorted square pyramidal around the nickel ion. The similarity between the solid reflectance spectrum of the octahedral $Ni(pydca)(tmen)\cdot 2H_2O$ species and that of the postulated pentacoordinate Ni(pydca)(tmen), Fig. 1, is not unusual. The main differences in the nickel(II) spectra for these symmetries lie in the magnitudes of the extinction coefficients. These values could not be determined for the latter complex since it was insoluble in solvents with low donor numbers.

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References

1 J. G. H. du Preez, M. Laing and B. J. A. M. van Brecht, *S. Afr. J. Chem., 28,* 220 (1975).
2 J. G. H. du Preez, B. J. A. M. van Brecht and R. F. van de Water, *S. Afr. J. Chem., 33,* 9 (1980).
3 J. F. de Wet, J. G. H. du Preez and B. J. A. M. van Brecht, *Inorg. Nucl. Chem., Letters, 10,* 935 (1974).
4 J. G. H. du Preez, B. J. A. M. van Brecht, R. F. van de Water and M. R. Caira, *J. Inorg. Nucl. Chem., 43,* 2011 (1981).
5 South African Patent, 1980, 6992.
6 C. N. Reilly and R. W. Schmid, *Anal. Chem., 30,* 947 (1958).
7 R. D. B. Fraser and Eikichi Suzuku, *Anal. Chem., 30,* 1771 (1958).
8 W. C. Hamilton, 'Statistics in Physical Science', Ronald Press, New York, 1964.
9 L. Ackerman, J. G. H. du Preez and M. L. Gibson, *Inorg. Chim. Acta, 5,* 539 (1971).
10 G. M. Sheldrick, SHELX-76, 'A Program for X-ray Crystal Structure Determination', University of Cambridge, 1976.
11 J. F. de Wet, The CRISTEP Desktop Plotter System for Molecular and Crystallographic Drawings, *J. Appl. Crystallogr., 13,* 625 (1980).

12 J. Babvich, K. P. Fivizzani, S. F. Pavkovic and J. N. Brown, *Inorg. Chem.*, *15,* 71 (1976).

13 N. W. Alcock and V. M.Tracy, *J. Chem. Soc. Dalton,* 2243 (1976).

14 M. Biagini Cingi, A. Chiesi Villa, G. Guastini and M. Nardelli, *Gazz. Chim. Ital.*, *101,* 825 (1971).

15 J. G. H. du Preez, H. E. Rohwer, B. J. A. M. van Brecht and M. R. Caira, submitted for publication in *J. Chem. Soc. Dalton* (1982).

16 G. J. McDougall and R. D. Hancock, *J. Chem. Soc. Dalton,* 654 (1980).

17 M. G. B. Drew and D. Rogers, *Chem. Comm.*, 476 (1965).

18 L. Pauling, 'The Nature of the Chemical Bond', Cornell Univ. Press, Ithaca, N.Y. (1960).

19 M. A. Bush and D. E. Fenton, *J. Chem. Soc. (A)*, 2446 (1971) and references therein.

20 D. P. Murtha and R. A. Walton, *Inorg. Chim. Acta, 8,* 279 (1974).

21 Unpublished Data.

22 S. Degetto, L. Baracco, M. Faggin and E. Celon, *J. Inorg. Nucl. Chem.*, *43,* 2413 (1981).