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Comparison of Complexes with Anionic and Neutral Amide Groups. Crystal and Molecular Structures of Bis N-(2-pyridyl)acetamide Complexes of Pd(II), Ni(II) and Zn(II)

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The crystal structure of the neutral complex $Pd(aap)_2$ of the title ligand shows a tetragonal Pd(II) with two trans ligands each chelated by the ring nitrogen and amide oxygen. The amide nitrogen is deprotonated and not coordinated. In the isomorphous $M(aapH)_2(NO_3)_2$ structures where M = Co(II), Ni(II), and Zn(II), there are two axial water molecules and again two trans ligands chelated as above but with a neutral amide nitrogen. For two of these complexes (M = Ni, Zn), the detailed molecular structures were determined. These complexes possess an amide C–O bond 0.04 Å shorter and an amide C–N bond 0.03 Å longer than are found in the $Pd(aap)_2$ complex. Crystal data for $Pd(aap)_2$: space group $P2_1/n$, Z = 2, a = 8.191(2), b = 4.859(1), c = 17.582(3) Å, β = 96.24(2)°, R = 3.2% for 1728 reflections. Crystal data for $[Zn(aapH)_2(H_2O)_2](NO_3)_2$: space group $P2_1/n$, Z = 2, a = 7.134(3), b = 10.266(6), c = 14.004(6) Å, β = 93.13(4)°, R = 6.0% for 1714 reflections. Crystal data for $[Ni(aapH)_2(H_2O)_2](NO_3)_2$: space group $P2_1/n$, Z = 2, a = 7.120(2), b = 10.170(2), c = 13.970(5) Å, β = 93.61(2)°, R = 3.2% for 1787 reflections. Crystal data for $[Co(aapH)_2(H_2O)_2(NO_3)_2$: space group $P2_1/n$, Z = 2, a = 7.113(6), b = 10.275(4), c = 14.045(7) Å, β = 93.6(1).

Introduction

It is now generally accepted that for neutral amide groups both protonation and metal ion coordination occur at the amide oxygen. Metal ion coordination takes place at the amide nitrogen only upon substitution for an amide hydrogen [1, 2]. Acidification of a nitrogen bound amide hydrogen upon substitution by a metal ion may be appreciable. Amide deprotonation in glycylglycine, which occurs with $pK_a \cong 15$ in the free ligand, drops to 4 in the Cu^{2+} complex and to less than 3 in the Pd^{2+} complex. It has been proposed that in the bis N-(2-pyridyl)acetamide (aapH) complex of Pd^{2+}, $Pd(aap)_2$, amide hydrogen deprotonation occurs with Pd^{2+} chelation at the pyridine nitrogen and acetamide oxygen; chelation including the deprotonated amide nitrogen remains unlikely due to the requirement for a 4-membered chelate ring [3]. Under basic conditions similar to those used to form $Pd(aap)_2$, Co^{2+}, Ni^{2+}, and Cu^{2+} precipitate their hydroxides.

We have prepared crystals of both $Pd(aap)_2$ from basic solutions and $M(aapH)_2(NO_3)_2$, where M = Co(II), Ni(II), and Zn(II) from neutral solutions. The last three complexes are isomorphous. Complete crystal structure determinations were carried out for two of the complexes (M = Ni(II) and Zn(II)), and these are compared with the structure of $Pd(aap)_2$. The crystal structure determination of the last complex confirms the previously proposed structure [3].

Experimental

Preparation of Complexes

The ligand N-(2-pyridyl)acetamide, aapH, was synthesized according to a published procedure [3]. Recrystallization from a mixture of dichloromethane and n-hexane gave colorless needles, m.p. 67–68.5 °C. The complex $Pd(aap)_2$ was prepared as described previously in a basic ethanol–water solvent [3]. The powdery yellow crystals were dried under high vacuum and dissolved in $CHCl_3$. After the solution was filtered to remove Pd^0, the solvent was allowed to evaporate. Crystals of sufficient quality for X-ray analysis formed easily. The water content of the final crystals varied from no water in the crystal used for diffraction to $1.6H_2O$ (NMR integration), all less than $4H_2O$ previously reported [3]. The ^1H NMR spectrum in $CDCl_3$ duplicates that already described [3] with the addition that the reported complex multiplet at 6.99 ppm was resolved in two multiplets at 6.92 ppm due to H(5) and at 7.13 ppm due to H(3). The solid blue Ni^{2+}, colorless Zn^{2+}, and or-

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ange Co^{2+} dinitrate complexes of aapH were prepared as previously described [3]. They were crystallized from concentrated aqueous solution without added acid or base at about pH 6.

Crystal Data for Bis(N-(2-pyridyl)acetamido)palladium(II)

$PdO_2N_4C_{14}H_{14}$, mol wt 377, space group $P2_1/n$, $Z = 2$, $a = 8.191(2)$ Å, $b = 4.859(1)$ Å, $c = 17.582(3)$ Å, $\beta = 96.24(2)°$, $V = 696$ Å^3, $\rho_{calc} = 1.80$ g cm^{-3}, $\rho_{obs} = 1.76$ g cm^{-3}, μ(MoKα) = 13.2 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (101) 0.23, $(\bar{1}0\bar{1})$ 0.23, $(10\bar{1})$ 0.295, $(\bar{1}01)$ 0.295, (010) 0.29, $(0\bar{1}0)$ 0.29, (001) 0.38, $(00\bar{1})$ 0.38; maximum, minimum transmission coefficients 0.69, 0.54.

Crystal Data for [Zn(aapH)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

$ZnO_8N_6C_{14}H_{14}$, mol wt 498, space group $P2_1/n$, $Z = 2$, $a = 7.134(3)$ Å, $b = 10.266(6)$ Å, $c = 14.004(6)$ Å, $\beta = 93.13(4)°$, $V = 1024$ Å^3, $\rho_{calc} = 1.61$ g cm^{-3}, $\rho_{obs} = 1.58$ g cm^{-3}, μ(MoKα) = 12.9 cm^{-1}, crystal dimensions (mm from centroid) $(1\bar{1}0)$ 0.38, $(\bar{1}\bar{1}0)$ 0.32, (101) 0.26, $(\bar{1}0\bar{1})$ 0.26, (011) 0.31, $(0\bar{1}\bar{1})$ 0.31, $(01\bar{1})$ 0.29, $(0\bar{1}1)$ 0.29, (001) 0.21, $(00\bar{1})$ 0.21, maximum, minimum transmission coefficients 0.81, 0.56.

Crystal Data for [Ni(aapH)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

$NiO_{10}N_6C_{14}H_{20}$, mol wt 491, space group $P2_1/n$, $Z = 2$, $a = 7.120(2)$ Å, $b = 10.170(2)$ Å, $c = 13.970(5)$ Å, $\beta = 93.61(2)°$, $V = 1010$ Å^3, $\rho_{calc} = 1.61$ g cm^{-3}, $\rho_{obs} = 1.58$ g cm^{-3}, μ(MoKα) = 10.3 cm^{-1}, crystal dimensions (mm from centroid) (100) 0.14, $(\bar{1}00)$ 0.14, (011) 0.10, $(0\bar{1}\bar{1})$ 0.10, $(01\bar{1})$ 0.10, $(0\bar{1}1)$ 0.10, miximum, minimum transmission coefficients 0.91, 0.87.

Crystal Data for [Co(aapH)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

$CoO_{10}N_6C_{14}H_{20}$, mol wt 491, space group $P2_1/n$, $Z = 2$, $a = 7.113(6)$ Å, $b = 10.275(4)$ Å, $c = 14.045(7)$ Å, $\beta = 93.6(1)°$, $V = 1025$ Å^3.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used, as previously described [4], to record the intensities for all non-equivalent reflections for which $1.5° < 2\theta < 60°$ for the Pd complex and $1.5° < 2\theta < 55°$ for the Zn and Ni complexes. Scan widths were calculated as (A + Btanθ), where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.6 and 0.35° respectively for all three complexes.

The intensities of four standard reflections, monitored at 100 reflection intervals for each complex, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 1849 independent intensities for the Pd complex, 1893 for the Zn complex, 1903 for the Ni complex, there were 1728, 1714 and 1787 with $F_0^2 > 3\sigma(F_0^2)$, where $\sigma(F_0^2)$ was estimated from counting statistics [5]. These data were used in the final refinement of the structural parameters.

Structure Determinations

[Pd(aap)$_2$] and [Zn(aapH)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

The space group, the volume of the unit cell and the anticipated molecular formulation of both the Pd and the Zn complexes requires that the metal atoms be in a special position at an inversion center in each case. The three-dimensional Patterson functions calculated from all intensity data confirmed this postulate. The intensity data were phased sufficiently well by these positional coordinates to permit location of the other nonhydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described [4]. Anisotropic temperature factors were introduced for all nonhydrogen atoms of both the complexes. Further Fourier difference functions permitted location of the hydrogens, which were included in the refinement for three cycles of least-squares and then held fixed. The models converged with $R = 3.2\%$, $R_w = 4.0\%$ for the Pd complex and $R = 6.0\%$, $R_w = 7.0\%$ for the Zn complex.

[Ni(aapH)$_2$(H$_2$O)$_2$](NO)$_3$)$_2$

The cell parameters indicate that the Ni and Co complexes are isomorphous with [Zn(aapH)$_2$(H$_2$O)$_2$](NO$_3$)$_2$. The refinement for the Ni complex was carried out using the atomic positions of the Zn analog as starting parameters. The model converged with $R = 3.2\%$, $R_w = 4.6\%$.

Final Fourier difference functions for all three complexes were featureless. Tables of the observed and calculated structure factor amplitudes are available[≠]. The principal programs used are as previously described [4].

Results and Discussion

Final positional and thermal parameters for bis(N-(2-pyridyl)acetamido)palladium(II), [Pd(aap)$_2$], are given in Table Ia. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted, and were derived from the inverse matrix in the course of least squares refinement calculations. Figure 1 is a stereoscopic pair view of the [Pd(aap)$_2$] molecule and of the molecular packing in the unit cell.

[≠] Supplementary material available. A listing of observed and calculated structure factors (24 pages).

TABLE Ia. Positional and Thermal Parameters and their Estimated Standard Deviations[a]. Pd(N-(2py)acetamide)$_2$.

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.0000(0)	0.0000(0)	0.0000(0)	2.62(1)	3.14(1)	2.22(1)	−0.149(7)	0.982(8)	−0.056(7)
O	−0.2091(2)	0.1604(5)	0.0257(1)	3.62(6)	5.4(1)	4.09(8)	1.08(7)	2.08(6)	1.08(8)
N(1)	0.0086(3)	−0.2564(4)	0.0922(1)	2.95(7)	3.30(8)	2.58(7)	−0.07(7)	0.93(6)	0.10(7)
N(2)	−0.2553(3)	−0.1189(5)	0.1302(1)	3.06(7)	2.77(9)	2.65(8)	0.18(8)	1.51(6)	0.26(8)
C(2)	−0.1133(3)	−0.2679(5)	0.1385(1)	3.52(9)	3.24(10)	2.77(8)	−0.58(8)	1.26(7)	−0.38(8)
C(3)	−0.0983(4)	−0.4452(7)	0.2013(2)	4.24(12)	4.25(11)	3.21(11)	−0.03(10)	1.61(9)	0.35(10)
C(4)	0.0368(4)	−0.6102(8)	0.2167(2)	4.59(12)	4.05(12)	3.30(10)	−0.07(12)	0.82(10)	0.58(11)
C(5)	0.1592(4)	−0.6021(8)	0.1693(2)	4.38(12)	4.56(12)	3.83(12)	0.57(13)	0.83(10)	1.05(12)
C(6)	0.1408(4)	−0.4237(8)	0.1081(2)	3.55(10)	4.59(11)	3.44(11)	0.51(11)	1.30(9)	0.66(11)
C(7)	−0.2920(3)	0.0731(7)	0.0783(2)	3.29(9)	3.99(10)	2.70(9)	−0.15(9)	1.21(8)	−0.40(9)
C(8)	−0.4500(4)	0.2256(7)	0.0831(2)	3.59(10)	4.98(14)	4.48(12)	0.48(10)	1.69(9)	0.05(12)
H(3)	−0.182(6)	−0.45(1)	0.234(3)	4.(1)					
H(4)	0.051(6)	−0.74(1)	0.262(3)	4.(1)					
H(5)	0.259(6)	−0.73(1)	0.179(3)	4.(1)					
H(6)	0.229(6)	−0.41(1)	0.075(3)	4.(1)					
H81	−0.537(6)	0.09(1)	0.093(3)	5.(1)					
H82	−0.504(6)	0.26(1)	0.028(3)	5.(1)					
H83	−0.429(6)	0.38(1)	0.108(3)	5.(1)					

[a] The form of the anisotropic thermal parameter is:
$\mathrm{Exp}[-(B_{11}.A^*.A^*.H.H + B_{22}.B^*.B^*.K.K + B_{33}.C^*.C^*.L.L)/4 + (B_{12}.A^*.B^*.H.K + B_{13}.A^*.C^*.H.L + B_{23}.B^*.C^*.K.L)/2]$.

TABLE II. Bond Lengths and Closest Interionic Contacts for [Pd(aap)$_2$] (A), [Zn(aap)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (B) and [Ni(aap)$_2$(H$_2$O)$_2$](NO$_3$)$_2$) (C).

	A	B	C
M–O	1.979(1)	2.058(4)	2.020(2)
M–O(W)		2.159(4)	2.096(2)
M–N(1)	2.039(1)	2.111(4)	2.079(3)
O–C(7)	1.278(2)	1.252(6)	1.229(4)
O(1N)–N(N)		1.231(6)	1.225(4)
O(2N)–N(N)		1.242(6)	1.244(4)
O(3N)–N(N)		1.228(6)	1.229(4)
N(1)–C(2)	1.358(1)	1.346(6)	1.328(4)
N(1)–C(6)	1.358(2)	1.333(7)	1.363(5)
N(2)–C(2)	1.364(2)	1.389(7)	1.407(4)
N(2)–C(7)	1.316(2)	1.329(6)	1.356(4)
C(2)–C(3)	1.395(2)	1.407(7)	1.398(5)
C(3)–C(4)	1.369(2)	1.374(8)	1.368(6)
C(4)–C(5)	1.372(2)	1.370(9)	1.379(6)
C(5)–C(6)	1.377(2)	1.358(8)	1.360(5)
C(7)–C(8)	1.502(2)	1.501(8)	1.497(5)
⟨C–H⟩	0.98	0.98	0.95
⟨N–H⟩		0.82	0.84
⟨O–H⟩		0.91	0.89
Pd–C(6)	3.508(2)[a]		
O–N(1)	3.481(4)[a]		
O–C(2)	3.453(4)[a]		
N(2)–C(3)	3.421(4)[b]		
C(3)–C(7)	3.453(4)[c]		
		Zn	Ni
O(1N)–N(2)		3.016(6)[d]	3.016(4)[d]
O(1N)–C(2)		3.014(7)[d]	3.008(5)[a]
O(2N)–N(2)		2.920(6)[e]	2.933(4)[e]
O(3N)–O(W)		2.843(6)[d]	2.807(4)[d]

Note →

TABLE III. Bond Angles (deg) for [Pd(aap)$_2$] (A), [Zn(aap)$_2$(H$_2$O)$_2$(NO$_3$)$_2$ (B) and [Ni(aap)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (C).

	A	B	C
O–M–O	180.0	180.0	180.0
O–M–O(W)		91.2(2)	90.0(1)
O–M–N(1)	90.87(4)	87.0(2)	87.2(1)
O(W)–M–O(W)		180.0	180.0
O(W)–M–N(1)		89.3(2)	88.9(1)
N(1)–M–N(1)	180.0	180.0	180.0
M–O–C(7)	125.2(1)	126.4(3)	126.9(2)
M–N(1)–C(2)	122.6(1)	123.9(3)	124.6(2)
M–N(1)–C(6)	119.2(1)	118.9(4)	118.4(2)
C(2)–N(1)–C(6)	118.2(1)	117.3(5)	117.0(3)
O(1N)–N(N)–O(2N)		118.0(5)	118.5(4)
O(1N)–N(N)–O(3N)		119.9(5)	120.6(4)
O(2N)–N(N)–O(3N)		122.1(5)	120.9(3)
C(2)–N(2)–C(7)	125.4(1)	129.6(4)	128.7(3)
N(1)–C(2)–N(2)	126.0(1)	121.4(4)	120.1(3)
N(1)–C(2)–C(3)	119.6(1)	122.0(5)	123.1(3)
N(2)–C(2)–C(3)	114.5(1)	116.6(5)	116.8(3)
C(2)–C(3)–C(4)	121.2(1)	118.3(6)	118.5(4)
C(3)–C(4)–C(5)	119.4(1)	119.3(5)	118.9(4)
C(4)–C(5)–C(6)	117.9(1)	119.1(6)	119.6(4)
N(1)–C(6)–C(5)	123.7(1)	124.0(6)	122.7(4)
O–C(7)–N(2)	129.6(1)	125.1(5)	123.9(3)
O–C(7)–C(8)	113.9(1)	118.5(5)	120.5(3)
N(2)–C(7)–C(8)	116.4(1)	116.4(5)	115.6(3)
O(2N)–H(N)–N(2)		167	169
O(2N)–H(W1)–O(W)		155	156
O(3N)–H(W2)–O(W)		136	143

[a] x, 1 + y, z [b] −x − 1, 1/2 + y, 1/2 − z [c] x, y − 1, z
[d] 1/2 − x, 1/2 − y, 1/2 − z [e] 1/2 + x, 1/2 − y, 1/2 + z

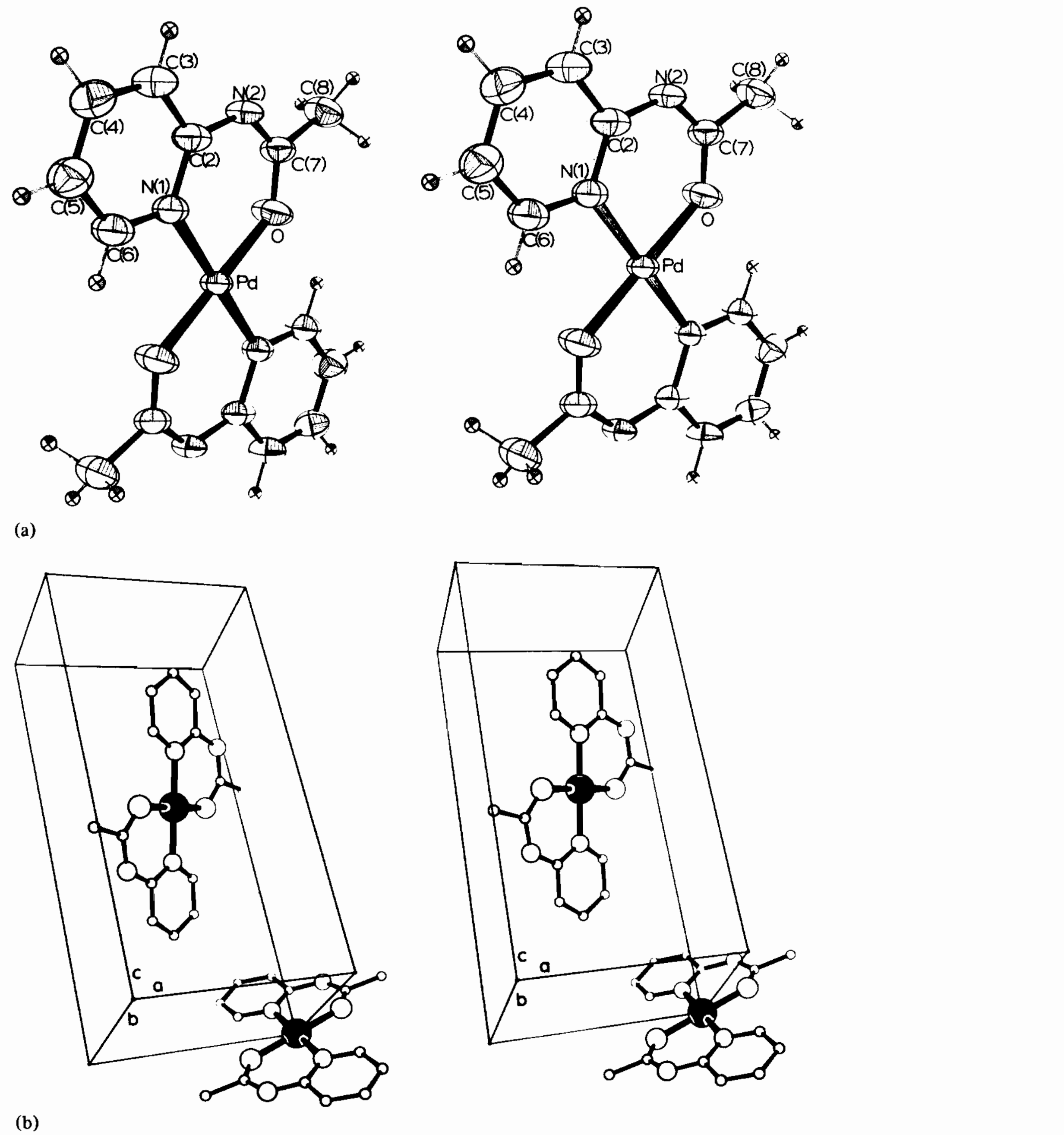

Fig. 1. (a) Stereoview of the molecular structure of Pd(aap)$_2$. (b) Stereoview of unit cell contents.

The complex consists of neutral monomeric molecules with no unusually close intermolecular approaches. The closest nonhydrogen intermolecular contact (3.421 Å) is between N(2), the acetamide nitrogen atom and a ring carbon, C(3), of a neighboring molecule. The coordination to the metal is trans and occurs via pyridine nitrogen and the oxygen atom of the acetamide group. The acetamide nitrogen atom is well separated from all the metal atoms, showing no tendency to coordinate.

The acetamide nitrogen is found to be deprotonated. There are four items of evidence for this: (a) The structure refined well enough to permit all the expected hydrogen atoms to be found, yet no hydrogen atom could be found on this nitrogen. (b) The absence of any counteranions in the unit cell requires deprotonation somewhere in the ligand to produce a neutral molecule. (c) The entire ligand, and in particular the chelating group N(1)–C(2)–N(2)–C(7)–O is highly planar (Table IV), indicative of the conjugation that would result from deprotonation. (d) The C–N bonds to this nitrogen have bond lengths characteristic of a bond order greater than one, which is also indicative of deprotonation.

The complex has essentially planar geometry overall. The PdO_2N_2 group is precisely planar, as required by crystallographic symmetry. The two pyridine rings are precisely parallel to one another and inclined at 3.5° to the central PdO_2N_2 plane. The chelating group N(1)–C(2)–N(2)–C(7)–O is closely planar and inclined at 4.8° to the central PdO_2N_2 plane. The metal atom is located 0.12 Å out of the N(1)–C(2)–N(2)–C(7)–O plane.

The atomic parameters, bond lengths and angles for the $[M(app)_2(H_2O)_2](NO_3)_2$ complexes are given in Tables Ib–III. Figure 2 shows a stereo view of the $[Ni(aapH)_2(H_2O)_2]^{2+}$ ion and the packing in the $[Ni(aapH)_2(H_2O)_2](NO_3)_2$ cell. The Zn(II) analog is quite similar and is therefore not drawn separately. The complexes each have two axially coordinated water molecules and trans aapH ligands chelated via the ring nitrogen and amide oxygen atoms. By contrast with $Pd(aap)_2$, the $[M(aapH)_2(H_2O)_2]^{2+}$ ions have relatively non-planar aapH ligands, for which the H atom on N(2) was located in each case. Atom N(2) lies off the plane made up of the remainder of the chelating group N(1)–C(2)–C(7)–O, by 0.16 Å when M = Zn and 0.17 Å for M = Ni. This chelating group bends away further from the central MO_2N_2 plane (18.5°, 19.4° for M = Zn, Ni respectively) than in the Pd(II) complex (4.8°). The $[M(aapH)(H_2O)_2]^{2+}$ coordination geometry approximates a regular octahedron. Distortions from this regular geometry are best indicated by the three equatorial planes of donor atoms, which are required, by crystallographic symmetry to be precisely planar, though not precisely square: these planes intersect at the metal atom and are nearly but not exactly orthogonal (89.3°, 88.8°, 87.0° for M = Zn, and 88.9°, 89.9°, 87.2° for M = Ni).

Bond angles in the Pd(II) complex when compared to the average for the Zn(II) and Ni(II) complexes show significant changes where the acetamide nitrogen is involved. The C(2)–N(2)–C(7) angle is 3.8°

TABLE IVa. Coefficients of Least-squares Planes for AX + BY + CZ = D.

Plane	Atoms	A	B	C	D	Distances from Plane (Å)
I	Pd, O, N(1)	−0.451	−0.692	−0.565	0	Pd, O, N(1) all 0.00
II	N(1), C(2), C(3), C(4), C(5), C(6)	−0.397	−0.720	−0.570	0.027	N(1) – 0.01, C(2) 0, C(3) 0, C(4) 0, C(5) 0, C(6), 0, N(2) 0.02
III	N(1), N(2), C(2), C(7), O	−0.386	−0.685	−0.618	−0.119	N(1) 0.02, N(2) 0.01, C(2) – 0.02, C(7) 0.01, O – 0.01, Pd 0.12, C(8) – 0.04
IV	O, N(1), N(2), C(2), C(3), C(4), C(5), C(6), C(7)	−0.394	−0.705	−0.590	−0.061	O – 0.06, N(1) 0.03, N(2) 0.05, C(2) 0.02, C(3) – 0.02, C(4) – 0.04, C(5) – 0.01, C(6) 0.02, C(7) 0, Pd 0.06, C(8) – 0.05

Interplanar Angles (deg)

I,II	I,III	I,IV	II,III
3.5	4.8	3.6	3.5

TABLE IVb. Coefficients for Least-squares Planes for AX + BY + CZ = D.

Plane	Atoms	A	B	C	D	Distances from Plane (Å)
I	Zn, O, N(1)	−0.631	−0.195	−0.751	0	Zn, O, N(1) all 0.00
II	N(1), C(2), C(3), C(4), C(5), C(6)	−0.424	−0.438	−0.793	−0.094	N(1) 0.01, C(2) – 0.01, C(3) 0, C(4) 0.01, C(5) 0, C(6) – 0.01, Zn 0.09
III	O, C(7), C(2), N(1)	−0.571	−0.473	−0.671	−0.441	O – 0.01, C(7) 0.02, C(2) – 0.02, N(1) 0.01, Zn 0.44, N(2) 0.16
IV	O, C(7), C(2), N(1), C(3), C(4), C(5), C(6)	−0.509	−0.452	−0.733	−0.419	O – 0.12, C(7) – 0.04, C(2) 0.15, N(1) 0.16, C(3) 0.03, C(4) – 0.09, C(5) – 0.10, C(6) 0.01, Zn 0.42, N(2) 0.22
V	Zn, O, O(W)	0.502	0.622	−0.601	0	Zn, O, O(W) all 0.00
VI	Zn, O(W), N(1)	0.597	−0.726	−0.341	0	Zn, O(W), N(1) all 0.00

Interplanar Angles (deg)

I,II	I,III	I,IV	I,V	I,VI	II,III	V,VI
18.5	17.0	16.4	89.3	88.8	11.2	87.0

smaller, while the two adjacent angles N(2)–C(2)–N(1) and N(2)–C(7)–O are 5.2° larger. The only other angles with a greater than 3° difference are O–C(7)–C(8) which is 5.6° smaller and O–M–N(1) which is 3.8° larger.

Bond lengths in the Pd(II) complex compared to the average in the Zn(II) and Ni(II) complexes exhibit the greatest differences when atoms from the amide group are included. The N(2)–C(2) and N(2)–C(7) bond lengths are 0.03 Å shorter while the

TABLE IVc. Coefficients of Least-squares Planes for AX + BY + CZ = D.

Planes	Atoms	A	B	C	D	Distances from Plane (A)
I	Ni, O, N(1)	−0.644	−0.177	−0.745	0	Ni, O, N(1) all 0.00
II	O, C(7), C(2), N(1)	−0.572	−0.493	−0.656	−0.490	O – 0.02, C(7) 0.03, C(2) – 0.02, N(1) 0.02, Ni 0.49, N(2) 0.17
III	N(1), C(2), C(3), C(4), C(5), C(6)	−0.411	−0.457	−0.789	−0.116	N(1) 0.02, C(2) – 0.01, C(3) 0, C(4) 0.01, C(5) – 0.01, C(6) – 0.01, Ni 0.12
IV	O, C(7), C(2), N(1), C(3), C(4), C(5), C(6)	−0.504	−0.473	−0.723	−0.472	O – 0.13, C(7) – 0.04, C(2) 0.15, N(1) 0.18, C(3) 0.03, C(4) – 0.10, C(5) – 0.12, C(6) 0.02, Ni 0.47, N(2) 0.24
V	Ni, O, O(W)	0.500	0.620	−0.604	0	Ni, O, O(W) all 0.00
VI	Ni, O(W), N(1)	0.592	−0.730	−0.341	0	Ni, O(W), N(1) all 0.00

Interplanar Angles (deg)

I,II	I,III	I,IV	I,V	I,VI	II,III	V,VI
19.4	21.1	18.9	88.9	89.9	12.2	87.2

TABLE Ib. Positional and Thermal Parameters and their Estimated Standard Deviations[a]. [Zn(N-(2-py)acetamide)$_2$(H$_2$O)$_2$]-(NO$_3$)$_2$.

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	0.0000(0)	0.0000(0)	0.0000(0)	3.30(4)	2.28(4)	2.42(4)	0.41(4)	0.63(3)	0.20(4)
O	−0.1640(8)	0.1516(5)	0.0433(4)	4.7(2)	2.9(2)	3.1(2)	0.9(2)	1.1(2)	0.1(2)
O(IN)	0.3225(12)	−0.1209(9)	0.4247(5)	8.3(4)	8.0(5)	4.0(3)	1.4(4)	−2.4(3)	0.3(3)
O(2N)	0.2188(11)	−0.0056(6)	0.3079(4)	8.5(4)	3.2(2)	3.9(2)	−0.4(3)	−0.5(3)	0.3(2)
O(3N)	0.2024(10)	−0.2156(6)	0.3006(5)	6.3(4)	3.8(3)	6.5(3)	−0.9(3)	0.4(3)	−1.5(3)
O(W)	0.2087(8)	0.0394(6)	0.1138(4)	4.9(3)	3.5(2)	2.9(2)	0.0(2)	−0.6(2)	0.4(2)
N(1)	0.1325(8)	0.1364(6)	−0.0868(4)	3.0(2)	2.6(2)	2.3(2)	−0.1(2)	0.3(2)	−0.3(2)
N(N)	0.2478(9)	−0.1150(6)	−0.3434(4)	3.4(3)	2.6(2)	2.9(2)	−0.3(2)	0.4(2)	−0.1(2)
N(2)	−0.1108(9)	0.2946(7)	−0.0778(4)	3.2(3)	3.3(3)	2.9(2)	0.7(2)	0.3(2)	0.5(2)
C(2)	0.058(1)	0.2525(7)	−0.1124(5)	3.1(3)	2.8(3)	2.0(2)	−0.2(3)	−0.3(2)	0.0(2)
C(3)	0.147(1)	0.3382(8)	−0.1738(6)	4.0(4)	3.4(3)	3.5(3)	−0.6(3)	−0.0(3)	0.8(3)
C(4)	0.317(1)	0.3015(9)	−0.2072(6)	4.1(4)	4.6(4)	3.9(3)	−1.0(3)	1.1(3)	0.8(3)
C(5)	0.394(1)	0.1846(10)	−0.1789(6)	3.9(3)	4.9(4)	4.5(4)	−0.4(3)	1.9(3)	0.1(4)
C(6)	0.299(1)	0.1070(8)	−0.1194(6)	4.0(3)	3.4(3)	4.2(3)	0.4(3)	1.2(3)	0.1(3)
C(7)	−0.198(1)	0.2553(7)	−0.0013(5)	3.1(3)	2.2(3)	2.8(3)	0.4(2)	0.0(2)	−0.1(2)
C(8)	−0.353(1)	0.3410(9)	0.0301(7)	5.2(4)	4.1(4)	5.1(4)	2.1(3)	1.3(3)	0.4(4)
H(N)	−0.16(1)	0.360(10)	−0.102(7)	7.(3)					
H(W1)	0.20(1)	−0.001(9)	0.177(6)	4.(2)					
H(W2)	0.27(1)	0.109(10)	0.113(7)	7.(3)					
H(3)	0.09(1)	0.429(8)	−0.188(6)	3.(2)					
H(4)	0.40(1)	0.360(9)	−0.234(6)	4.(2)					
H(5)	0.51(1)	0.162(9)	−0.203(6)	5.(2)					
H(6)	0.35(1)	0.026(9)	−0.105(6)	5.(2)					
H(81)	−0.47(1)	0.308(10)	0.018(7)	7.(3)					
H(82)	−0.35(1)	0.445(9)	0.013(7)	6.(2)					
H(83)	−0.32(1)	0.340(11)	0.100(8)	8.(3)					

[a] The form of the anisotropic thermal parameter is:
$\mathrm{Exp}[-(B_{11}.A^*.A^*.H.H + B_{22}.B^*.B^*.K.K + B_{33}.C^*.C^*.L.L)/4 + (B_{12}.A^*.B^*.H.K + B_{13}.A^*.C^*.H.L + B_{23}.B^*.C^*.K.L)/2]$.

C(7)–O bond length is 0.04 Å longer. No other non-metal–ligand bond lengths differ by more than 0.02 Å.

In other amides metal ions coordinated to neutral amide groups have little effect on bond lengths and angles [2, 6]. In the Pd(II) complex with a deprotonated amide nitrogen, compared to the Ni(II) and Zn(II) complexes with a neutral amide group, the amide C–N bond becomes 0.03 Å shorter with more double bond character while the amide C–O bond becomes 0.04 Å longer with less double bond character. This shortening and lengthening of bonds to the amide group carbon atom in the amide deprotonated Pd(II) complex is slightly greater (0.01 Å) than similar changes found in other amides upon metal ion substitution for an amide hydrogen [2]. Thus loss of a nitrogen-bound amide hydrogen produces the major change in amide group bond lengths while only a minor reversal occurs upon metal ion coordination to a deprotonated amide nitrogen. That metal ion coordination produces only a fraction of the effect of protonation at the same site has been noted in other crystal structures [7]. Even multiply charged cations are much less polarizing than the proton with its high charge density [8].

The deprotonated but uncoordinated amide nitrogen found in the Pd^{2+} complex is unlikely to occur with ordinary amides such as those found in peptides. The ligand aapH is an acetanilide or an amide of a weakly basic aniline nitrogen. The pK_a of aapH was not determinable by potentiometric titration in water but is likely to be about 11 or about 4 log units lower than for ordinary aliphatic amides. The deprotonated, uncoordinated amide nitrogen in the Pd(II) complex is accountable by the enforced chelate stereochemistry and the weak amide nitrogen basicity.

Acknowledgements

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Supplementary Material Available

A listing of observed and calculated structure factors (24 pages).

TABLE Ic. Positional and Thermal Parameters and their Estimated Standard Deviations[a]. $[Ni(N\text{-}2\text{-}py)acetam)_2(H_2O)_2](NO_3)_2$.

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.0000(0)	0.0000(0)	0.0000(0)	2.34(2)	1.99(2)	1.74(2)	0.30(2)	0.53(2)	0.15(2)
O	−0.1558(4)	0.1513(3)	0.0451(2)	3.6(1)	2.4(1)	2.55(9)	0.67(9)	1.15(8)	0.36(9)
O(1N)	0.3243(6)	−0.1184(4)	0.4258(2)	7.5(2)	6.2(2)	3.69(14)	1.30(18)	−2.04(14)	0.11(15)
O(2N)	0.2140(5)	−0.0074(3)	0.3066(2)	7.4(2)	3.1(1)	3.36(12)	0.04(14)	−0.33(13)	0.68(12)
O(3N)	0.2056(5)	−0.2187(3)	0.3023(3)	5.7(2)	3.4(1)	5.53(16)	−0.76(13)	0.29(14)	−1.37(13)
O(W)	0.2059(4)	0.0387(3)	0.1102(2)	3.5(1)	3.2(1)	2.48(10)	−0.20(10)	−0.23(9)	0.09(9)
N(1)	0.1306(4)	0.1350(3)	−0.0857(2)	2.4(1)	2.5(1)	2.1(1)	0.0(1)	0.56(9)	0.0(1)
N(N)	0.2486(4)	−0.1160(3)	0.3446(2)	2.7(1)	2.9(1)	2.7(1)	−0.1(1)	0.65(10)	0.1(1)
N(2)	−0.1140(4)	0.2922(3)	−0.0789(2)	2.7(1)	2.7(1)	2.6(1)	0.6(1)	0.43(10)	0.7(1)
C(2)	0.0579(5)	0.2503(4)	−0.1130(2)	2.3(1)	2.6(1)	1.9(1)	−0.1(1)	0.1(1)	0.1(1)
C(3)	0.1444(6)	0.3354(4)	−0.1754(3)	3.5(2)	3.1(2)	3.1(2)	−0.3(1)	0.3(1)	1.0(1)
C(4)	0.3145(6)	0.2999(5)	−0.2078(3)	3.6(2)	4.4(2)	3.3(2)	−1.0(2)	1.1(1)	0.9(2)
C(5)	0.3950(6)	0.1828(5)	−0.1770(3)	3.0(2)	4.6(2)	3.9(2)	−0.3(2)	1.7(1)	0.1(2)
C(6)	0.3025(6)	0.1038(4)	−0.1171(3)	3.0(2)	3.2(2)	3.4(2)	0.4(1)	1.2(1)	0.2(1)
C(7)	−0.1981(5)	0.2523(4)	0.0005(3)	2.5(1)	2.3(1)	2.6(1)	0.2(1)	0.3(1)	−0.2(1)
C(8)	−0.3509(6)	0.3402(5)	0.0324(3)	4.1(2)	3.5(2)	4.7(2)	1.7(2)	1.6(2)	0.4(2)
H(N)	−0.161(7)	0.360(5)	−0.105(4)	6.(1)					
H(W1)	0.202(6)	−0.002(5)	0.172(3)	5.(1)					
H(W2)	0.257(8)	0.110(6)	0.113(4)	7.(1)					
H(3)	0.097(6)	0.424(4)	−0.191(3)	4.(1)					
H(4)	0.388(6)	0.360(4)	−0.235(3)	4.(1)					
H(5)	0.505(7)	0.161(5)	−0.196(3)	5.(1)					
H(6)	0.358(6)	0.026(5)	−0.100(3)	5.(1)					
H(81)	−0.470(9)	0.304(6)	0.014(4)	9.(2)					
H(82)	−0.360(7)	0.438(6)	0.017(4)	8.(1)					
H(83)	−0.329(9)	0.346(6)	0.106(4)	9.(2)					

[a] The form of the anisotropic thermal parameter is:
$Exp[-(B_{11}.A^*.A^*.H.H + B_{22}.B^*.B^*.K.K + B_{33}.C^*.C^*.L.L)/4 + (B_{12}.A^*.B^*.H.K + B_{13}.A^*.C^*.H.L + B_{23}.B^*.C^*.K.L)/2]$.

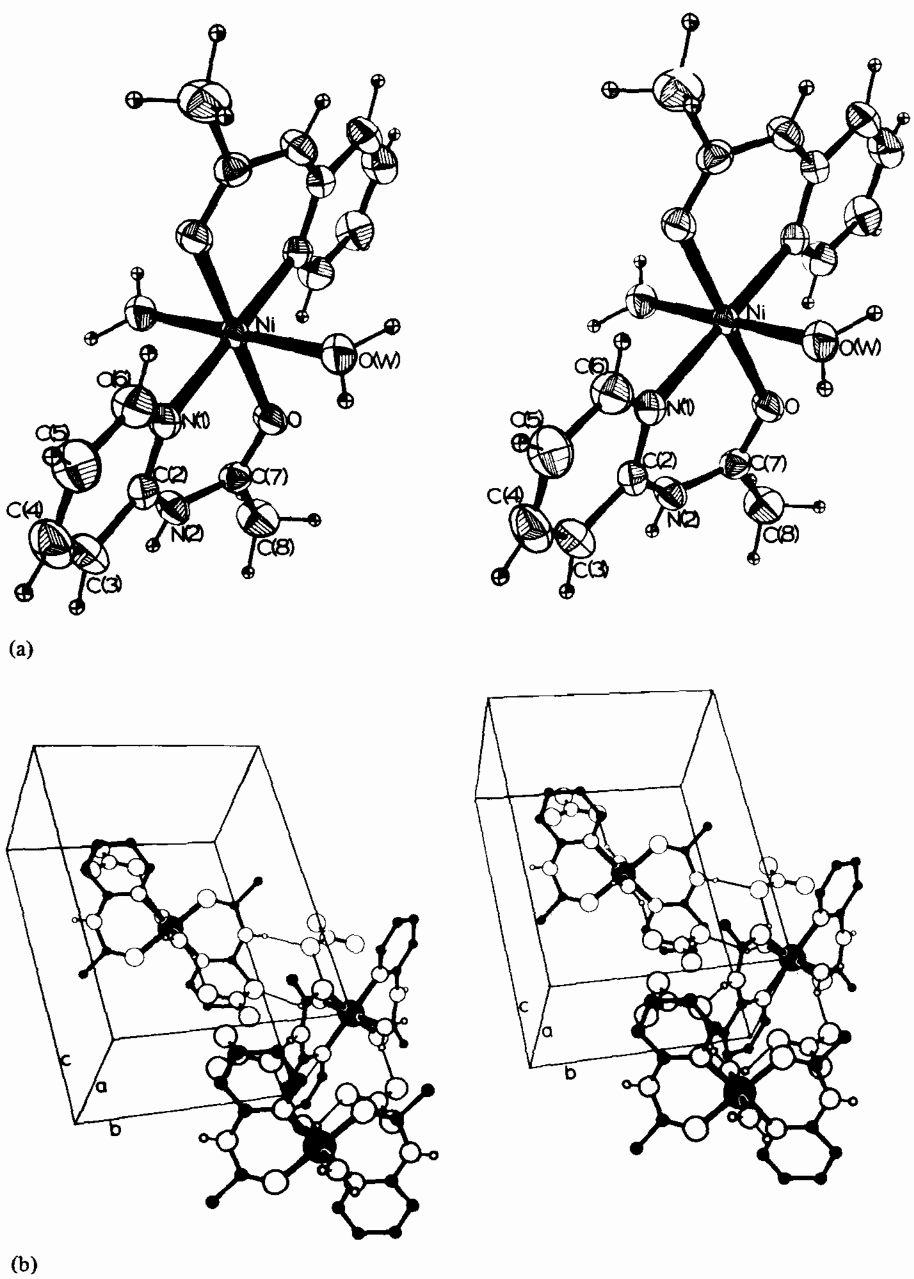

Fig. 2. (a) Stereoview of the [Ni(aapH)$_2$(H$_2$O)$_2$]$^{2+}$ ion. (b) Stereoview of the ionic packing and hydrogen-bonding in the [Ni(aapH)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ lattice (and in that of its isomorphous Zn(II) analog).

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