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Note

Structures of a monomeric and a dimeric Ni(II) complex containing 2-acetylpyrrole

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Abstract

The structures of two derivatives of Ni(II) containing 2-acetylpyrrole are reported. The first compound is a dimer containing four 2-acetylpyrrole and two isopropylamine molecules, with the nickel centers bridged by carbonyl oxygen atoms from two of the four 2-acetylpyrrole groups. The second derivative is a monomer containing two n-butylamine and two 2-acetylpyrrole molecules, with the latter arranged in a planar fashion around the nickel center. Crystals of the dimer are triclinic with space group $P\bar{1}$ with $a=8.281(2)$, $b=9.694(2)$, $c=11.495(2)$ Å, $\alpha=110.08(3)$, $\beta=105.57(3)$, $\gamma=99.35(3)°$, $V=801.1(2)$ Å^3 and $Z=1$. Crystals of the monomer are triclinic with space group $P\bar{1}$ with $a=5.626(2)$, $b=9.803(2)$, $c=10.792(2)$ Å, $\alpha=74.96(2)$, $\beta=81.81(2)$, $\gamma=83.34(2)°$, $V=566.9(2)$ Å^3 and $Z=1$.

Keywords: Crystal structures; Nickel complexes; Schiff base complexes; Dimeric complexes

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1. Introduction

Crystal structures have been reported for a number of metal ion complexes containing Schiff base derivatives of two related α-substituted pyrrole ligands, 2-acetylpyrrole and pyrrole-2-aldehyde. Complexes of Cu(II) and Zn(II) [1–3] with imine derivatives of 2-acetylpyrrole, and those of Cu(II) [4–6], Zn(II) [7,8], Co(II) [9] and Ni(II) [10–12] with imines derived from pyrrole-2-aldehyde have been structurally characterized. Fewer structures are known in which complexation occurs directly between the metal ion and 2-acetylpyrrole or pyrrole-2-aldehyde; these include a square planar Cu(II) compound containing two chelated 2-acetylpyrrole molecules [3], and a distorted square planar mixed-ligand product containing one Schiff base and one 2-acetylpyrrole per Cu(II) center [1].

We now report the syntheses and structures of two novel 2-acetylpyrrole derivatives of Ni(II): one a dimer, $Ni_2(2ac)_4(ipa)_2$, (2ac = 2-acetylpyrrole, ipa = isopropylamine), and the second a monomer, $Ni(2ac)_2(n\text{-}bu)_2$ (n-bu = n-butylamine). These compounds can be obtained by slightly altering the reaction conditions for the formation of the corresponding Schiff base complexes with Ni(II) [13]. In the dimer, two of the four 2-acetylpyrrole molecules are bonded to one nickel atom only, while the other two bridge between the metal centers through their carbonyl oxygen atoms. Structures of relatively few dimeric Ni(II) compounds with oxygen bridges have been reported; these include complexes with tri-, tetra- and hexadentate ligands which also bridge the metal centers [14–17], as well as Ni(II) dimers containing either pyridine or piperidine and which are bridged by acetylacetonate oxygen atoms [18]. In addition, a binuclear Ni(II) complex containing a polyimidazole ligand has been structurally characterized [19], which acts as a model of the active site of urea amido hydrolase isolated from jack beans and which contains two Ni(II) ions per molecule of protein [20]. The monomer reported herein is structurally similar to a square planar Cu(II) complex containing two 2-acetylpyrrole molecules [3], but no corresponding Ni(II) compounds have been reported.

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2. Experimental

2.1. Preparation of $Ni_2(2ac)_4(ipa)_2$

A mixture of 2-acetylpyrrole (10 mmol) and $NiSO_4 \cdot 6H_2O$ (10 mmol) was slurried in 40 ml of isopropylamine. The resulting green solid was extracted with methylene chloride to yield the crude product. The product was purified by recrystallization from methylene chloride/pentane solution. *Anal.* Calc. for $Ni_2(C_6H_6NO)_4 \cdot 2C_3H_9N$: C, 53.9; H, 6.3; N, 12.6. Found: C, 54.1; H, 6.2; N, 12.1%. IR spectra exhibited peaks characteristic of ν(N–H) at 3314 and 3251 cm^{-1}, and a ν(C=O) band at 1538 cm^{-1}.

2.2. Preparation of $Ni(2ac)_2(n\text{-}bu)_2$

A mixture of 2-acetylpyrrole (10 mmol) and $NiSO_4 \cdot 6H_2O$ (10 mmol) was slurried in 40 ml of 50% n-butylamine/H_2O to yield a blue solid. The reaction product was extracted with methylene chloride to remove insoluble nickel hydroxide, and purple crystals of the complex were then obtained from methylene chloride/pentane solution. These were mechanically separated from the green dimeric product also formed from solution. *Anal.* Calc. for $Ni(C_6H_6NO)_2 \cdot 2C_4H_{11}N$: C, 57.0; H, 8.1; N, 13.3. Found: C, 56.6; H, 8.3; N, 13.6%. IR spectra exhibited peaks characteristics of ν(N–H) at 3333 and 3263 cm^{-1}, and a ν(C=O) band at 1549 cm^{-1}.

2.3. X-ray structure determination and refinements

Crystallographic data are presented in Table 1. All data were collected on a Siemens R3/V four-circle diffractometer at ambient temperature using Mo Kα radiation ($\lambda = 0.71073$ Å). The scan range was 1.2°, and the scan rate was varied between 1.5 and 15.0°/min. Data were collected using θ–2θ scan mode for 2θ between 3.0 and 55.0°. Three standard reflections were monitored every 50 reflections and no significant decay was observed. No absorptions corrections were applied. All calculations and plots were made using SHELXTL Plus [21]. Hydrogen atom positions were calculated with C–H and N–H bond lengths set at 0.96 and 0.90 Å, respectively. All non-hydrogen atoms are described with anisotropic thermal parameters. Final electron difference maps showed no significant features. Thermal ellipsoid plots (50% probability) of the compounds are shown in Figs. 1 and 2 and indicate the numbering scheme used. See also Section 4.

Table 1
Crystallographic data

	$Ni_2(2ac)_4(ipa)_2$	$Ni(2ac)_2(n\text{-}bu)_2$
Formula	$C_{30}H_{42}N_6O_4Ni_2$	$C_{20}H_{34}N_4O_2Ni$
Formula weight	668.2	421.2
Space group	$P\bar{1}$	$P\bar{1}$
Color	green	purple
Size (mm)	0.42×0.18×0.12	0.63×0.53×0.26
a (Å)	8.281(2)	5.626(2)
b (Å)	9.694(2)	9.803(2)
c (Å)	11.495(2)	10.792(2)
α (°)	110.08(3)	74.96(2)
β (°)	105.57(3)	81.81(2)
γ (°)	99.35(3)	83.34(2)
V (Å^3)	801.1(2)	566.9(2)
Z	1	1
ρ_{calc} (Mg m^{-3})	1.385	1.234
μ (mm^{-1})	1.218	0.876
h,k,l measured	$\pm h, \pm k, \pm l$	$h, \pm k, \pm l$
No. independent data	3700	2276
No observed data [a]	2779	2019
No. paramctcrs	191	125
Data/parameter	14.5:1	16/2:1
Residual ED, e Å^{-3}	0.39, −0.41	0.49, −0.47
R [b]	0.032	0.039
R_w [c]	0.039	0.054
S [d]	1.31	1.26

[a] ($I > 3\sigma(I)$).

[b] $R = [\Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|]$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|wF_o|^2]^{1/2}$.

[d] $S = \Sigma w(|F_o| - |F_c|)^2$/no. obs. ref. − no. parameters).

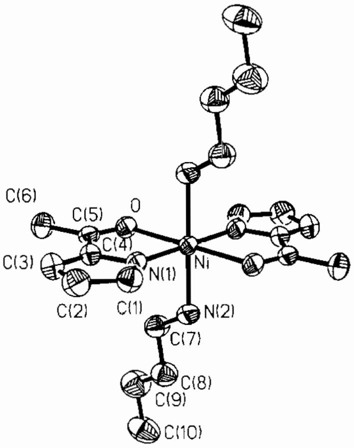

Fig. 1. Structure of $Ni(2ac)_2(n\text{-}bu)_2$.

3. Results and discussion

Primary amines employed in the syntheses of the monomer and dimer act to deprotonate the pyrrole nitrogen atom prior to complexation with Ni(II). Care must be taken to minimize amine concentration in these reactions, as a large excess results in the formation of Schiff base complexes; this was the subject of an earlier report [13]. Temperature and concentration dependent monomer–dimer equilibria involving nickel(II) complexes of some *o*-quinone monoximes have been reported recently, including calculations of some equilibrium constants and enthalpies and entropies of dissociation [22]. Work is underway in our laboratory to study the

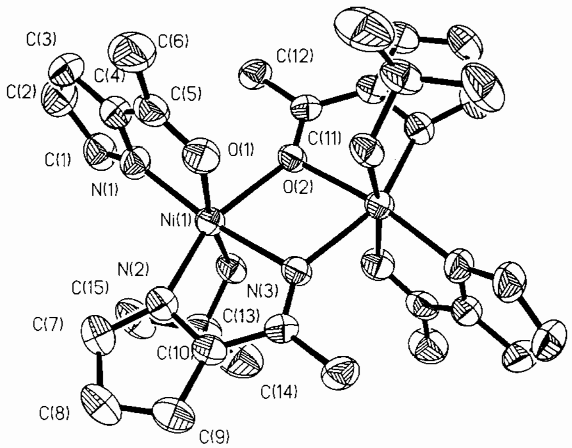

Fig. 2. Structure of $Ni_2(2ac)_4(ipa)_2$.

Table 2
Bond lengths (Å) and angles (°) in the coordination sphere

$Ni_2(2ac)_2(ipa)_2$		$Ni(2ac)_2(n\text{-}bu)_2$	
Ni(1)–O(1)	2.130(2)	Ni–O	2.126(2)
Ni(1)–O(2)	2.191(2)	Ni–N(1)	2.060(2)
Ni(1)–N(1)	1.995(2)	Ni–N(2)	2.118(2)
Ni(1)–N(2)	2.025(2)		
Ni(1)–N(3)	2.098(2)		
Ni(1)–O(2A)	2.125(2)		
O(1)–Ni(1)–O(2)	86.7(1)	O–Ni–N(1)	79.8(1)
O(1)–Ni(1)–N(1)	80.5(1)	O–Ni–N(2)	93.3(1)
O(2)–Ni(1)–N(1)	98.2(1)	N(1)–Ni–N(2)	92.2(1)
O(1)–Ni(1)–N(2)	93.0(1)	N(1)–Ni–O(A)	100.2(1)
O(2)–Ni(1)–N(2)	157.0(1)	N(2)–Ni–O(A)	86.7(1)
N(1)–Ni(1)–N(2)	104.5(1)	N(2)–Ni–N(1A)	87.8(1)
O(1)–Ni(1)–N(3)	170.0(1)		
O(2)–Ni(1)–N(3)	83.2(1)		
N(1)–Ni(1)–N(3)	101.2(1)		
N(2)–Ni(1)–N(3)	96.1(1)		
O(1)–Ni(1)–O(2A)	88.4(1)		
O(2)–Ni(1)–O(2A)	77.5(1)		
N(1)–Ni(1)–O(2A)	168.3(1)		
N(2)–Ni(1)–O(2A)	79.5(1)		
N(3)–Ni(1)–O(2A)	89.2(1)		

equilibria between monomeric and dimeric products in the n-butylamine case.

Bond lengths and angles in the coordination sphere of the two complexes are given in Table 2. The monomer has an octahedral core composed of two chelated 2-acetylpyrrole molecules and two coordinated amines. The nickel is located at the crystallographic center of symmetry. The equitorial plane exhibits similar bond angles and distances to that of a previously reported square planar copper complex [3]. Ni–O and Ni–N bond distances are longer than the corresponding Cu–O and Cu–N distances in the copper complex (2.036 and 1.913 Å, respectively), and can be rationalized by the inductive effects of the coordinated *trans* butylamine groups in the nickel compound.

Each Ni(II) ion in the dimer has a distorted octahedral geometry. There is a crystallographic center of symmetry relating the two metal centers. R_{int} for the dimer is 0.019. The Ni–O–Ni bond angle is 102.5(1)°, and the bridging 2-acetylpyrrole ligands are nearly co-planar with the central Ni_2O_2 ring. The non-bridging 2-acetylpyrrole ligands form a dihedral angle of 92.9° with this ring. The Ni–O distances in the central core differ by 0.066(3) Å. The Ni–Ni distance of 3.366(2) Å lies between the shorter distances (2.891–3.240 Å) [16–18] and a longer distance (3.422 Å) [19] reported in the literature. Investigations of the magnetic behavior of dimeric and monomeric complexes are planned.

4. Supplementary material

Fractional coordinates in Supplemental Table S1, bond distances in Supplemental Table S2, bond angles in Supplemental Table S3, thermal parameters in Supplemental Table S4, calculated positions of hydrogen atoms in Supplemental Table S5, and observed and calculated structure factors in Supplemental Table S6 are available from the authors on request.

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