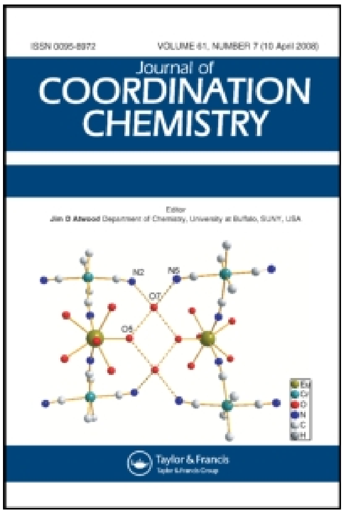

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Synthesis, Characterization and Crystal Structure of a Nickel(II) Schiff Base Complex Derived from Acetylacetone and Ethylenediamine

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NICKEL(II) SCHIFF BASE COMPLEX DERIVED FROM ACETYLACETONE AND ETHYLENEDIAMINE

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The square-planar nickel (II) complex of composition $[Ni(bae)] \cdot \frac{1}{2} H_2O$ (**1**) [where H_2bae is bis(acetylacetone)ethylenediamine] has been synthesized by [2 + 1] template condensation of acetylacetone and ethylenediamine in the presence of $NiCl_2 \cdot 6H_2O$ and characterized. An X-ray structure determination of the complex has been completed. Average Ni–N and Ni–O distances are, respectively, 1.86(2) Å and 1.849(14) Å. N $\cdots$ N bite distance and bite angle are 2.627(6) Å and 87.2(2)°, respectively, for the five-membered chelate ring. The water molecule forms hydrogen bonds with O atoms of two complex molecules.

Keywords: Template synthesis; Nickel(II); bis(acetylacetone)ethylenediamine; NMR; X-ray structure

INTRODUCTION

Metal complexes with asymmetric compartmental ligands have been the focus of extensive studies because of their applications in several area of chemical research [1–4]. The Schiff base bis(acetylacetone)ethylenediamine **I**, H_2bae [4,4′-(1,2-ethanediyldinitrilo)-bis(2-pentanone)] obtained from the condensation between two moles of acetylacetone and one mole of ethylenediamine, has been shown both in the solid state [5] and in solution [6] to have an enaminoketone structure with intramolecular hydrogen bonding. Structural studies of complexes with metals in various coordination environments have been reported, *viz*, [OV(bae)], square pyramidal [7], $[Cu(bae)] \cdot CH_3NH_3ClO_4$, planar [8], $[Cu(bae) \cdot H_2O]$, pyramidal [9], $[Cu(bae)] \cdot \frac{1}{2} H_2O$ tetragonal pyramidal [10], $[C_6H_5 \cdot Co^{III}(bae) \cdot H_2O]$, distorted octahedral [11], $[CH_3 \cdot Co^{III}(bae)]$, distorted rectangular-based pyramidal [12], $[CH_2{=}CH \cdot Co(bae) \cdot H_2O]$, distorted octahedral [13] and $[Co(bae)] \cdot C_6H_6$, square planar [14]. No crystal structure of a Ni^{II}(bae) complex has been reported, although the crystal structures of several other Ni(II) Schiff base

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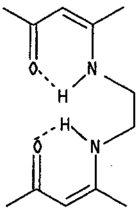
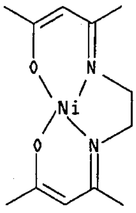
complexes have been described [15]. Nickel-containing systems have importance particularly in biological redox enzymes [16,17] and can catalyze the oxidation of guanine residues in DNA leading to strand scission [18]. Complexes with cores of the type MN_2O_2 are themselves reversible dioxygen carriers [19]. In continuation of our studies on Schiff base complexes [20,21], we report here the template synthesis, characterization and crystal structure of a monomeric square planar Ni(II) complex.



I (H_2bae)



Ni(bae) 1

EXPERIMENTAL

All chemicals were of reagent grade and were used as received. Acetylacetone, ethylenediamine and $NiCl_2 \cdot 6H_2O$ were obtained from Aldrich and Merck. Solvents were purified by standard methods [22].

Physical Measurements

Elemental analysis was performed by the University of North London, London, UK. Molar conductance in 10^{-3} mol dm^{-3} MeOH solution was measured using a Global DCM-900 digital conductivity meter. IR spectra was recorded on a Perkin-Elmer 1720 FT spectrometer in nujol mull. The EI mass spectrum was recorded at 70 eV on a VG Autospec mass spectrometer. The electronic spectrum in 10^{-4} mol dm^{-3} MeOH solution was obtained using a Shimadzu UV-160A recording spectrophotometer. ^1H and $^{13}C\{^1H\}$NMR spectra were recorded on a 500 MHz Brucker NMR instrument and chemical shifts are relative to $SiMe_4$.

Preparation of [Ni(bae)] · $\frac{1}{2}H_2O$

To a boiling solution of $NiCl_2 \cdot 6H_2O$ (0.951 g, 4.00 mmol) and acetylacetone (0.80 g, 8.0 mmol) in methanol (20 cm^3), a methanolic solution of ethylenediamine (0.240 g, 4.00 mmol) was added slowly with constant stirring and the mixture was boiled under reflux for 4 h. The resulting brown solution was cooled to room temperature and allowed to stand for 7 days during which brown plates formed. The crystals were filtered off, washed with methanol and dried in air, yield, 1.80 g (77%). *Anal.* Calc. for $C_{12}H_{18}N_2O_2Ni \cdot 0.5(H_2O)$ (%): C, 49.65; H, 6.55; N, 9.65. Found: C, 49.81; H, 6.45; N, 9.72; MS (EI) (*m*/*z*): 280 (100) [M–0.5 H_2O]$^+$, 169(84) [M–Me–MeCOCHCMeNH]$^+$, 69(25); IR (cm^{-1}): 3551–3495 [ν(OH)]; 1632 [ν(CO)]; 1590 [ν(C=N)]; 954, 816 [$\rho_\tau(CH_2)$]; electronic spectrum (nm) (ε, M^{-1}cm^{-1}) (MeOH): 567(72), 351(5740), 269(14160); ^1HNMR ($CDCl_3$): δ 4.89 (s, 2H, CH), 3.01

TABLE I Crystal data and structure refinement details for [Ni(bae)] $\cdot \frac{1}{2}H_2O$

Empirical formula	$C_{12}H_{18}N_2NiO_2 \cdot 0.5(H_2O)$
Formula weight	290.0
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$ (No. 15)
Unit cell dimensions	$a = 22.1948(8)$ Å $b = 8.3967(5)$ Å $\beta = 127.962(2)^\circ$ $c = 17.8458(9)$ Å
Volume	2622.1(2) Å^3
Z	8
Density (calculated)	1.47 Mg/m^3
Absorption coefficient	1.48 mm^{-1}
Crystal size	$0.3 \times 0.2 \times 0.1$ mm^3
Theta range for data collection	3.47–27.88°
Index ranges	$-28 \leq h \leq 29$, $-10 \leq k \leq 11$, $-22 \leq l \leq 23$
Reflections collected	10198
Independent reflections	3111[R(int) = 0.059]
Reflections with $I > 2\sigma(I)$	2456
Data/restraints/parameters	3111/0/167
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.034$, $wR2 = 0.072$
R indices (all data)	$R1 = 0.050$, $wR2 = 0.078$
Largest diff. peak and hole	0.29 and -0.40 e Å^{-3}

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U(eq)
Ni	758(1)	1483(1)	1248(1)	21(1)
N(1)	255(1)	2372(2)	50(1)	23(1)
N(2)	1457(1)	651(2)	1102(1)	22(1)
O(1)	94(1)	2305(2)	1445(1)	27(1)
O(2)	1218(1)	573(2)	2431(1)	27(1)
C(1)	−556(1)	2998(3)	811(2)	28(1)
C(2)	−825(1)	3333(2)	−99(2)	27(1)
C(3)	−417(1)	3083(2)	−459(2)	25(1)
C(4)	712(1)	2321(3)	−291(2)	28(1)
C(5)	1229(1)	886(3)	145(2)	28(1)
C(6)	2060(1)	−230(2)	1719(2)	25(1)
C(7)	2267(1)	−630(3)	2621(2)	27(1)
C(8)	1847(1)	−254(3)	2917(2)	26(1)
C(9)	−1000(1)	3447(3)	1161(2)	40(1)
C(10)	−772(1)	3692(3)	−1444(2)	33(1)
C(11)	2558(1)	−862(3)	1478(2)	33(1)
C(12)	2075(1)	−820(3)	3857(2)	39(1)
O(3)	0	−685(4)	2500	45(1)

(s, 4H, CH_2), 1.86, 1.87 (d, CH_3), 1.66 (s, H_2O); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.7 (CO), 164.5 (CN), 99.5 (CH), 52.9 (CH_2), 24.3 (CH_3CO), 21.1 (CH_3CN); Λ_M (10^{-3} M, MeOH, 298 K): 34 S cm^2 mol^{-1}.

TABLE III Selected bond lengths (Å) and bond angles (°) for complex **1** with estimated standard deviations in parentheses

Bond lengths			
Ni–O(1)	1.8465(14)	C(1)–C(2)	1.370(3)
Ni–O(2)	1.8514(14)	C(1)–C(9)	1.503(3)
Ni–N(1)	1.8553(17)	C(2)–C(3)	1.414(3)
Ni–N(2)	1.8594(17)	C(3)–C(10)	1.505(3)
N(1)–C(3)	1.319(2)	C(4)–C(5)	1.508(3)
N(1)–C(4)	1.469(3)	C(6)–C(7)	1.415(3)
N(2)–C(6)	1.319(2)	C(6)–C(11)	1.508(3)
N(2)–C(5)	1.465(3)	C(7)–C(8)	1.362(3)
O(1)–C(1)	1.301(2)	C(8)–C(12)	1.502(3)
O(2)–C(8)	1.301(2)		
Bond angles			
O(1)–Ni–O(2)	83.24(6)	N(2)–C(5)–C(4)	108.53(18)
O(1)–Ni–N(1)	94.85(7)	N(2)–C(6)–C(7)	122.4(2)
O(2)–Ni–N(1)	177.46(6)	N(2)–C(6)–C(11)	120.4(2)
O(1)–Ni–N(2)	177.71(7)	C(7)–C(6)–C(11)	117.27(18)
O(2)–Ni–N(2)	94.70(7)	C(8)–C(7)–C(6)	124.38(19)
N(1)–Ni–N(2)	87.23(7)	O(2)–C(8)–C(7)	125.1(2)
C(3)–N(1)–C(4)	120.29(18)	O(2)–C(8)–C(12)	113.60(19)
C(3)–N(1)–Ni	126.83(16)	C(7)–C(8)–C(12)	121.30(19)
C(4)–N(1)–Ni	112.76(12)	O(1)–C(1)–C(9)	114.2(2)
C(6)–N(2)–C(5)	119.63(18)	C(2)–C(1)–C(9)	121.36(19)
C(6)–N(2)–Ni	126.85(15)	C(1)–C(2)–C(3)	125.04(19)
C(5)–N(2)–Ni	113.09(12)	N(1)–C(3)–C(2)	121.6(2)
C(1)–O(1)–Ni	126.11(15)	N(1)–C(3)–C(10)	121.0(2)
C(8)–O(2)–Ni	126.41(14)	C(2)–C(3)–C(10)	117.38(18)
O(1)–C(1)–C(2)	124.4(2)	N(1)–C(4)–C(5)	107.96(18)

X-Ray Structure Determination

Crystals were grown as brown plates by slow evaporation from methanol solution. Data were obtained on a Nonius Kappa CCD diffractometer with Mo$K\alpha$ radiation. Further information is given in Table I. An empirical absorption correction was applied ($T_{\mathrm{min}}/T_{\mathrm{max}}$, 0.65/0.76). The structure was solved and refined using SHELX-97 [23]. Nonhydrogen atoms were refined anisotropically with H atoms in riding mode. The ORTEP-3 programme [24] was used to prepare the molecular drawings. Atomic coordinates and equivalent isotropic displacement parameters are given in Table II. Selected bond lengths and angles are listed in Table III.

Supplementary material including anisotropic displacement parameters for nonhydrogen atoms, hydrogen coordinates and isotropic displacement parameters and torsion angles are available on request from the authors.

RESULTS AND DISCUSSION

Synthesis and Properties

Template condensation of 2,4-pentanedione (acetylacetone) with ethylenediamine in the presence of $NiCl_2 \cdot 6H_2O$ in methanol yields a red–brown complex of composition [Ni(bae)]$\cdot \frac{1}{2}H_2O$ (**1**). The molar conductance value in MeOH is low compared to values reported [25] for 1 : 1 electrolytes (85–110 $\mathrm{S\,cm^2\,mol^{-1}}$) suggesting that it is a nonelectrolyte. Elemental analysis agreed well with the formulation. The EI mass spectrum is dominated by a peak at *m*/*z* 280 due to $[M-\frac{1}{2}\ H_2O]^+$. The fragmentation pattern exhibits features due to $[M–Me–MeCOCHCMeNH]^+$. Calculated and observed isotopic patterns for $C_{12}H_{18}N_2O_2Ni$ are in good agreement.

IR spectra of the complex show no N–H stretching frequency, confirming that all the nitrogens are tertiary. Bands at 1632 and $1590\,cm^{-1}$ are attributable to ν(CO) and ν(C=N) vibrations, respectively. The region generally assigned to the CH_2-rocking modes [26] has bands at *ca.* 816 and $950\,cm^{-1}$, suggesting that the ethylene bridge has the *gauche* conformation, as confirmed by the crystal structure determination. Bands at 3551 and $3495\,cm^{-1}$ are indicative of intermolecular hydrogen bonding.

The electronic absorption spectrum shows λ_{max} at 506 nm (ε $72\,M^{-1}\,cm^{-1}$) in $CHCl_3$ solution (cf λ_{max} 511 nm (71) in H_2O and 492 nm in $MeNO_2$ for the square planar Ni(II) complex with N–Me_4–cyclam [27]). Bands at 351 and 269 nm are due to charge transfer and intra-ligand transitions respectively.

The ^1H NMR spectrum of the complex is almost identical to that of the ligand, H_2bae [6]. The methyl signal is a doublet. It is probable that the lower field signal is due to the methyl groups adjacent to the C–O since these would be slightly less shielded than those near the C–N groups. The =CH– and CH_2 protons are shifted by 0.11 and 0.41 ppm, respectively, relative to those in the ligand. A sharp singlet at 1.66 ppm is due to protons in water molecules bound by hydrogen bonding. The $^{13}C\{^1H\}$NMR spectrum shows six unique carbon peaks consistent with the ligand structure.

Crystal Structure of [Ni(bae)] · $\frac{1}{2}H_2O$ (1)

An ORTEP view of the complex **1** with the atom numbering scheme is shown in Fig. 1. The water molecule lies on a crystallographic 2-fold axis and forms hydrogen bonds

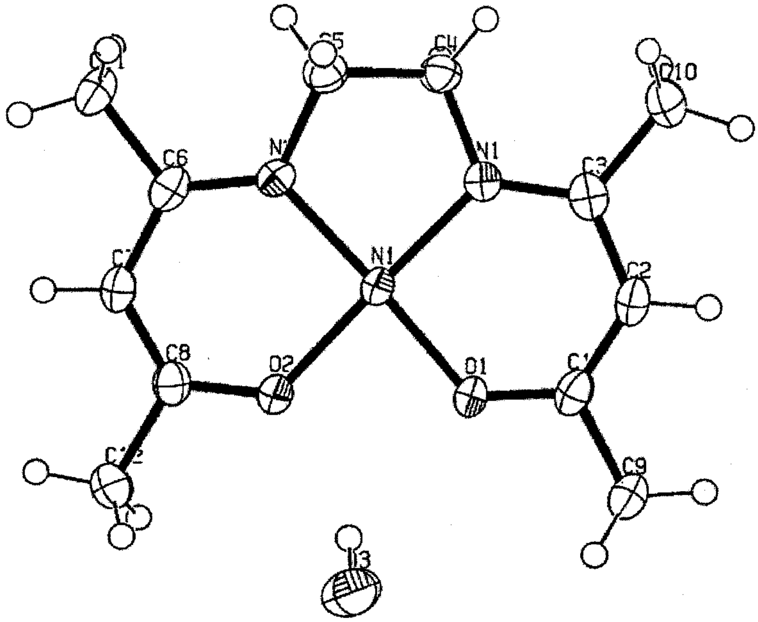


FIGURE 1 Molecular structure of the complex [Ni(bae)] · $\frac{1}{2}H_2O$.

of length 2.98 Å with atoms O(2) and O(2)′ of the two complex molecules. The ligand bae is dianionic and tetradentate and forms a square planar nickel(II) complex (sum of bond angles 360.02(7)°). The average Ni–N (1.86(2) Å) bond distance is not significantly different from that in [Ni($Me_2Ac_2H_2$malen)] **2** [15] {mean 1.836(5) Å} and falls in the order (1.86–1.94 Å) normally observed for square planar nickel(II) complexes of tetaazamacrocycles [28–30]; the Ni–O distance, 1.849(14) Å is also the same as that in **2**, 1.854(5) Å. The two NiNCCCO rings are coplanar and the nonplanar ethylenediamine ring adopts the usual *gauche* conformation consistent with the infrared data. The bite distances and angles are a measure of the macrocyclic hole size. In the five-membered chelate ring the N(1) ··· N(2) bite distance is 2.63(6) Å, which falls in the range, *ca.* 2.6–2.7 Å, generally observed. However, the bite angle 87.2(2)° is significantly shorter than those reported in the literature (92–96°) for the same chelate ring. C–O distances in the complex [1.301(2) Å] are significantly longer than those [1.245(4) and 1.242(4) Å] in the free ligand and C(1)–C(2) distances [1.370(3) and 1.362(3) Å] significantly shorter [cf 1.441(5) and 1.440(6) Å in H_2bae]. The C(2)–C(3) distance, 1.414(3) Å, is longer in the complex [cf 1.393(5) Å in H_2bae] and the C–N distance [1.319(2) Å] shorter [cf 1.329(3) and 1.333(3) Å in H_2bae], but in view of the experimental uncertainties we cannot be sure of the significance.

M–O and M–N distances in bae complexes are affected only slightly by hydrogen bonding. Neglecting the effect of coordination type, the following average values are obtained: Ni–O 1.849 Å, Ni–N 1.857 Å; Co–O 1.886 Å, Co–N 1.881 Å; Cu–O 1.923 Å, Cu–N 1.933 Å; V–O 1.951 Å, V–N 2.054 Å. M–O distances follow the same order as those in corresponding acetylacetonato compounds.

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