

1,2-Diaminobenzene Adducts of Nickel(II) 1,3-Diketonates: Their Role in Dibenzotetraaza[14]annulene Macrocyclic Formation

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Abstract

The attempted preparation of the macrocyclic ligand, 6,8,15,17-tetraphenyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine from 1,2-diaminobenzene, 1,3-diphenyl-1,3-propanedione, and nickel(II) acetate via a template condensation is unsuccessful because of severe steric interactions in the desired product. The product isolated from this reaction, in high yield, is the bis(1,2-diaminobenzene) adduct of bis(1,3-diphenyl-1,3-propanedionato)nickel(II).

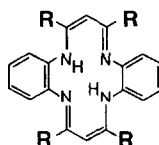
Crystals of the adduct are monoclinic with $a = 7.425(1)$, $b = 12.221(3)$, $c = 19.194(3)$ Å, $\beta = 97.01^\circ$, $Z = 2$, $V = 1728.7$ Å³, and space group $P2_1/n$. The structure was solved by the heavy atom method and difference Fourier techniques, and refined by the block-diagonal least-squares method to a final R of 0.0379 for 2218 reflections with $I > 2\sigma(I)$. An empirical absorption correction was made via ψ -scan of 5 reflections with 2θ -values between 5 and 90° , and χ close to 90° . The compound consists of a square planar Ni(II)–O₄ array with two molecules of axially coordinated diamine. The monodentate *trans* arrangement of the diamine molecules gives the compound the overall pseudo-octahedral geometry that is common to adducts of metal 1,3-diketonates.

The 6,8,15,17-tetramethyl macrocycle is readily formed via template condensation when the diketone employed is 2,4-pentanedione. The bis(1,2-diaminobenzene) adduct of bis(2,4-pentanedionato)nickel(II) has also been prepared. A small amount of macrocycle can be detected by refluxing this latter adduct in alcohol. The principal product is (1,2-diaminobenzene)tetrakis(2,4-pentanedionato)dinickel(II).

Introduction

Our recent research has been concerned with the electrochemical properties of dibenzotetraaza[14]-

annulene macrocycles and their potential use as catalysts [1–4]. An aspect of this effort has been an attempt to design specific and new macrocycles. This has led us to undertake a mechanistic study of the synthesis of this class of molecules. Of particular interest was the tetraphenyl macrocycle, 6,8,15,17-tetraphenyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine (**1a**). Malik *et al.* had reported the preparation of the iron(III) complex of this macrocycle via a template synthesis using FeCl₃ [5]. However, we have recently reexamined this product and have shown that it was actually the bis-diamine adduct of the iron(III) 1,3-diketonate [6]. We chose to investigate similar reactions utilizing nickel(II), typically a better ‘template metal’, and now report the product obtained from the attempted template preparation of **1a**.



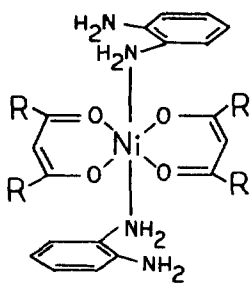
1a, R = Ph

1b, R = CH₃

Attempts to prepare the tetraphenyl macrocycle via standard literature procedures employed in the synthesis of the tetramethyl or dimethyl-diphenyl analogs [7, 8] resulted in the isolation of only the diamine adduct (**2a**). No evidence of the macrocycle was observed.

The 6,8,15,17-tetramethyl macrocycle (**1b**) is readily formed when 2,4-pentanedione is used in the template condensation [7]. Since the presence of the nickel(II) 1,3-diketonate adduct during macrocycle formation has not been noted, the bis(1,2-diaminobenzene) adduct of bis(2,4-pentanedionato)nickel(II) (**2b**) was also prepared. Jager's original synthesis of the tetramethyl macrocycle involved heating a neat mixture of bis(2,4-pentanedionato)nickel(II) dihydrate and 1,2-diaminobenzene [9].

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2a, R = Ph
2b, R = CH₃

Compounds **2a** and **2b** are readily prepared from the same components used in macrocycle synthesis. An investigation of these diamine adducts was therefore undertaken to determine their significance in macrocycle formation.

Experimental

Synthesis

All starting materials are commercially available. Microanalyses were performed by Atlantic Microlab Inc., Atlanta, Ga.

Preparation of bis(1,3-diphenyl-1,3-propanedionato)nickel(II)bis(1,2-diaminobenzene) (2a)

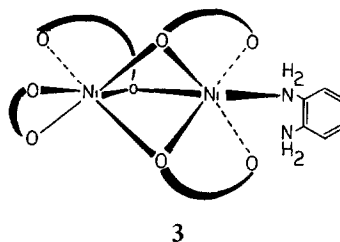
Nickel acetate tetrahydrate (6.56 g, 26.4 mmol) and 1,2-diaminobenzene (6.40 g, 59.2 mmol) were warmed in dry ethanol (200 ml) for 30 min. A solution of 1,3-diphenyl-1,3-propanedione (11.2 g, 49.8 mmol) in ethanol (200 ml) was added. The adduct **2a** precipitated within a few minutes. The reaction mixture was stirred until it had cooled to room temperature. The green solid (15.9 g, 88.5%) was collected and washed with ethanol. Material suitable for elemental analysis and crystallography was obtained via recrystallization from ethanol; melting point (m.p.) = 221–223 °C. *Anal.* Calc. for C₄₂H₃₈N₄NiO₄: C, 69.92; H, 5.31; N, 7.77. Found: C, 69.66; H, 5.38; N, 7.82%.

Preparation of bis(2,4-pentanedionato)nickel(II)-bis(1,2-diaminobenzene) (2b)

Nickel acetate tetrahydrate (2.61 g, 10.5 mmol) and 1,2-diaminobenzene (2.22 g, 20.6 mmol) were stirred in methanol (100 ml) for 10 min. A solution of 2,4-pentanedione (2.0 ml, 20 mmol) in methanol (10 ml) was added. The adduct **2b** precipitated within a few minutes. The light blue solid (1.06 g, 23.0%) was collected and washed with methanol; m.p. = 241–243 °C. *Anal.* Calc. for C₂₂H₃₀N₄NiO₄: C, 55.84; H, 6.39; N, 11.84. Found: C, 55.71; H, 6.48; N, 12.07%.

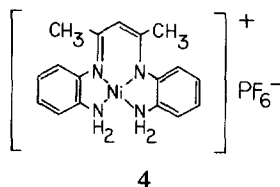
Preparation of (1,2-diaminobenzene)tetrakis-(2,4-pentanedionato)dinickel(II) (3)

Compound **2b** (2.37 g, 5.01 mmol) was refluxed in dry ethanol (100 ml) for 45 min. The light blue solid (1.02 g, 65.4%) was collected and washed with ethanol; m.p. = 293–295 °C (dec). *Anal.* Calc. for C₂₆H₃₆N₂Ni₂O₈: C, 50.21; H, 5.83; N, 4.50. Found: C, 49.96; H, 5.86; N, 4.46%.



Isolation of the macrocyclic intermediate [N,N''-(1,3-dimethyl-1,3-propanediylidene)bis(1,2-benzenediaminato)-N,N',N',N'']nickel(II) (4)

Compound **2b** (4.84 g, 10.2 mmol) and nickel acetate tetrahydrate (2.49 g, 10.0 mmol) were refluxed in dry ethanol for 72 h. The reaction mixture was filtered hot to remove compound **3** (1.26 g, 39.7%). The filtrate solvent was removed by rotary evaporation and the oily residue applied to an alumina column. The macrocycle was isolated by elution with chloroform (48.9 mg, 1.2%). Elution using chloroform was continued until all colored by-products were removed and the column was stripped with methanol. The methanol solution was added dropwise to an aqueous solution of ammonium hexafluorophosphate that had been neutralized to pH 7. The crude salt of the intermediate was collected and washed with water. ¹H NMR (d₆-acetone) was in agreement with the literature [10].



Spectroscopic Measurements

Infrared spectra were recorded on a Perkin-Elmer 1430 Ratio Recording Infrared Spectrometer using Nujol mulls and sodium chloride plates. The deuterated compounds were prepared by suspending the solid adducts (100 mg) in CH₃OD (2 ml) and stirring at room temperature until the solvent had evaporated.

TABLE I. Crystal Data

Formula	C ₄₂ H ₃₈ N ₄ NiO ₄
Molecular weight	721.50 g/mol
Cell dimensions	
<i>a</i>	7.425(1) Å
<i>b</i>	12.221(3) Å
<i>c</i>	19.184(3) Å
β	97.01°
<i>V</i>	1728.7 Å ³
Space group	<i>P</i> 2 ₁ / <i>n</i> (monoclinic)
<i>Z</i>	2
<i>D_c</i>	1.386 g/cm ³
λ	1.54178 Å
Temperature	24 °C
Scan type	ω -2 θ
Scan range	2° + dispersion
Scan speed	variable between 4° and 29° min ⁻¹
Octants measured	$\bar{h}kl, hkl$
Background	stationary for 1/2 scan time on each side of peak
Standard reflections	one after 50 measurements
No. measured	2473
No. used	2218 with <i>I</i> > 2 σ (<i>I</i>)
Secondary extinction coefficient	1.8 × 10 ⁻²
μ	11.9 cm ⁻¹
<i>R</i>	0.0379
<i>R_w</i>	0.0474

Structural Determination*

Large green needles of compound **2** were obtained by slowly cooling a solution of the compound in dry ethanol.

Collection of X-ray data

All data reported here were collected using an automated four-circle diffractometer, Nicolet R3M/ μ , equipped with a Cu X-ray tube, a graphite monochromator, and a pulse height analyzer. Lattice parameters, given in Table I, were obtained using the setting angles of 20 reflections with 2 θ values between 40° and 53°. Intensity data were collected using parameters summarized in Table I. An empirical absorption correction was made via ψ -scan of reflections with 2 θ values between 5 and 90°, and χ close to 90°. The minimum and maximum transmission factors were 0.63 and 0.69 respectively.

Solution and Refinement

The nickel(II) atom is constrained to lie on a center of inversion and was, therefore, placed at the origin. The rest of the atoms, including hydrogens, were obtained from successive difference Fourier

TABLE II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U^a</i>
Ni	0	0	0	35(1)
O(1)	-608(2)	1115(1)	-759(1)	39(1)
O(2)	-1016(2)	949(1)	718(1)	42(1)
C(1)	-1308(3)	2045(2)	-666(1)	33(1)
C(2)	-1720(3)	2469(2)	-32(1)	39(1)
C(3)	-1597(3)	1931(2)	608(1)	35(1)
C(4)	-2238(3)	2496(2)	1223(1)	38(1)
C(5)	-2957(3)	1900(2)	1732(1)	46(1)
C(6)	-3604(4)	2399(2)	2289(1)	59(1)
C(7)	-3506(4)	3511(2)	2358(1)	64(1)
C(8)	-2737(4)	4128(2)	1874(1)	65(1)
C(9)	-2116(3)	3615(2)	1303(1)	50(1)
C(10)	-1850(3)	2703(2)	-1317(1)	36(1)
C(11)	-1637(4)	3835(2)	-1329(1)	50(1)
C(12)	-2284(4)	4418(2)	-1922(1)	66(1)
C(13)	-3179(4)	3892(2)	-2496(1)	65(1)
C(14)	-3363(3)	2775(2)	-2493(1)	56(1)
C(15)	-2680(3)	2186(2)	-1907(1)	44(1)
C(16)	3076(3)	1750(2)	141(1)	41(1)
N(1)	2644(3)	681(2)	376(1)	47(1)
C(17)	3514(3)	1871(2)	-539(1)	43(1)
N(2)	3766(3)	924(2)	-930(1)	58(1)
C(18)	3795(3)	2912(2)	-783(1)	52(1)
C(19)	3677(3)	3806(2)	-368(2)	60(1)
C(20)	3265(4)	3692(2)	305(2)	64(1)
C(21)	2954(3)	2655(2)	560(1)	55(1)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalised *U_{ij}* tensor.

calculations. The structure was refined by the block-diagonal least-squares method by assigning anisotropic temperature factors to non-hydrogen atoms and isotropic temperature factors to the hydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma^2(F) + 0.00053F^2)$. The largest shift in a parameter in the last cycle of refinement was 0.21. The largest peak in the final difference Fourier was 0.20 e/Å³.

All calculations were performed on a Data General micro-eclipse desktop computer using the Nicolet SHELXTL crystallographic computing package. Drawings were made on a Nicolet ZETA-8 plotter.

The final positional parameters and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table II. Pertinent bond distances and angles are given in Table III. The atom numbering scheme is shown in Fig. 1.

Results and Discussion

The bis(1,2-diaminobenzene) adduct of bis(1,3-diphenyl-1,3-propanedionato)nickel(II) is a green solid which forms after the addition of diketone to a

*This crystal structure was determined initially by E. Sinn (University of Virginia) but all information was misplaced. It was then redetermined independently at North Carolina State University.

TABLE III. Bond Angles (°) and Bond Lengths (Å)

O(1)–Ni–O(2)	92.1(1)	O(1)–Ni–N(1)	95.5(1)
O(2)–Ni–N(1)	87.2(1)	O(1)–Ni–O(1A)	180.0(1)
O(2)–Ni–O(1A)	87.9(1)	N(1)–Ni–O(1A)	84.5(1)
O(1)–Ni–O(2A)	87.9(1)	O(2)–Ni–O(2A)	180.0(1)
N(1)–Ni–O(2A)	92.8(1)	O(1A)–Ni–O(2A)	92.1(1)
O(1)–Ni–N(1A)	84.5(1)	O(2)–Ni–N(1A)	92.8(1)
N(1)–Ni–N(1A)	180.0(1)	O(1A)–Ni–N(1A)	95.5(1)
O(2A)–Ni–N(1A)	87.2(1)	Ni–O(1)–C(1)	124.5(1)
Ni–O(2)–C(3)	124.8(1)	O(1)–C(1)–C(2)	126.4(2)
O(1)–C(1)–C(10)	115.9(2)	C(2)–C(1)–C(10)	117.6(2)
C(1)–C(2)–C(3)	126.9(2)	C(1)–C(2)–H(2)	114.0(12)
C(3)–C(2)–H(2)	118.5(12)	O(2)–C(3)–C(2)	125.0(2)
O(2)–C(3)–C(4)	115.8(2)	C(2)–C(3)–C(4)	119.2(2)
C(3)–C(4)–C(5)	120.3(2)	C(3)–C(4)–C(9)	121.6(2)
C(5)–C(4)–C(9)	118.1(2)	C(4)–C(5)–C(6)	121.5(2)
C(4)–C(5)–H(5)	119.9(14)	C(6)–C(5)–H(5)	118.6(14)
C(5)–C(6)–C(7)	120.0(2)	C(5)–C(6)–H(6)	118.5(14)
C(7)–C(6)–H(6)	121.6(14)	C(6)–C(7)–C(8)	120.1(2)
C(6)–C(7)–H(7)	124.7(13)	C(8)–C(7)–H(7)	115.2(13)
C(7)–C(8)–C(9)	119.4(2)	C(7)–C(8)–H(8)	116.1(16)
C(9)–C(8)–H(8)	124.3(16)	C(4)–C(9)–C(8)	120.8(2)
C(4)–C(9)–H(9)	119.3(14)	C(8)–C(9)–H(9)	119.9(14)
C(1)–C(10)–C(11)	121.8(2)	C(1)–C(10)–C(15)	119.2(2)
C(11)–C(10)–C(15)	118.9(2)	C(10)–C(11)–C(12)	119.8(2)
C(10)–C(11)–H(11)	121.8(13)	C(12)–C(11)–H(11)	118.4(13)
C(11)–C(12)–C(13)	120.4(2)	C(11)–C(12)–H(12)	116.0(19)
C(13)–C(12)–H(12)	123.6(19)	C(12)–C(13)–C(14)	120.1(2)
C(12)–C(13)–H(13)	119.0(15)	C(14)–C(13)–H(13)	120.7(15)
C(13)–C(14)–C(15)	119.7(2)	C(13)–C(14)–H(14)	121.5(15)
C(15)–C(14)–H(14)	118.6(15)	C(10)–C(15)–C(14)	121.0(2)
C(10)–C(15)–H(15)	115.7(16)	C(14)–C(15)–H(15)	123.0(16)
N(1)–C(16)–C(17)	118.7(2)	N(1)–C(16)–C(21)	121.1(2)
C(17)–C(16)–C(21)	120.1(2)	Ni–N(1)–C(16)	118.2(1)
Ni–N(1)–H(1A)	104.4(18)	C(16)–N(1)–H(1A)	113.4(19)
Ni–N(1)–H(1B)	92.2(24)	C(16)–N(1)–H(1B)	123.5(24)
H(1A)–N(1)–H(1B)	101.5(31)	C(16)–C(17)–N(2)	118.4(2)
C(16)–C(17)–C(18)	118.7(2)	N(2)–C(17)–C(18)	122.8(2)
C(17)–N(2)–H(2A)	112.3(15)	C(17)–N(2)–H(2B)	116.3(18)
H(2A)–N(2)–H(2B)	107.3(23)	C(17)–C(18)–C(19)	121.1(2)
C(17)–C(18)–H(18)	118.8(13)	C(19)–C(18)–H(18)	120.0(13)
C(18)–C(19)–C(20)	120.5(2)	C(18)–C(19)–H(19)	119.8(16)
C(20)–C(19)–H(19)	119.6(16)	C(19)–C(20)–C(21)	119.4(2)
C(19)–C(20)–H(20)	115.3(16)	C(21)–C(20)–H(20)	124.8(16)
C(16)–C(21)–C(20)	120.2(2)	C(16)–C(21)–H(21)	116.9(14)
C(20)–C(21)–H(21)	123.0(14)		
Ni–O(1)	2.005(1)	Ni–O(2)	2.018(1)
Ni–N(1)	2.173(2)	Ni–O(1A)	2.005(1)
Ni–O(2A)	2.018(1)	Ni–N(1A)	2.173(2)
O(1)–C(1)	1.271(2)	O(2)–C(3)	1.284(2)
C(1)–C(2)	1.391(3)	C(1)–C(10)	1.499(3)
C(2)–C(3)	1.388(3)	C(2)–H(2)	0.903(20)
C(3)–C(4)	1.494(3)	C(4)–C(5)	1.377(3)
C(4)–C(9)	1.379(3)	C(5)–C(6)	1.368(4)
C(5)–H(5)	0.919(23)	C(6)–C(7)	1.367(4)
C(6)–H(6)	0.847(21)	C(7)–C(8)	1.374(4)
C(7)–H(7)	1.007(24)	C(8)–C(9)	1.388(4)
C(8)–H(8)	0.954(20)	C(9)–H(9)	0.931(24)
C(10)–C(11)	1.393(3)	C(10)–C(15)	1.375(3)

(continued)

TABLE II. (continued)

C(11)–C(12)	1.379(3)	C(11)–H(11)	0.955(21)
C(12)–C(13)	1.375(4)	C(12)–H(12)	0.905(24)
C(13)–C(14)	1.371(4)	C(13)–H(13)	0.977(25)
C(14)–C(15)	1.380(3)	C(14)–H(14)	1.000(26)
C(15)–H(15)	0.903(28)	C(16)–N(1)	1.431(3)
C(16)–C(17)	1.391(3)	C(16)–C(21)	1.377(3)
N(1)–H(1A)	0.857(28)	N(1)–H(1B)	0.825(35)
C(17)–N(2)	1.404(3)	C(17)–C(18)	1.382(3)
N(2)–H(2A)	0.863(24)	N(2)–H(2B)	0.885(28)
C(18)–C(19)	1.362(4)	C(18)–H(18)	1.073(26)
C(19)–C(20)	1.370(4)	C(19)–H(19)	0.937(27)
C(20)–C(21)	1.388(4)	C(20)–H(20)	1.081(30)
C(21)–H(21)	0.980(26)		

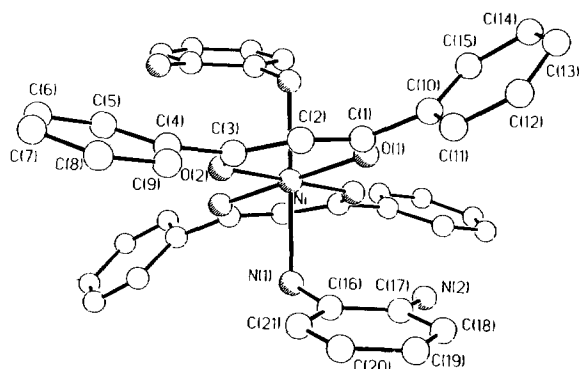


Fig. 1. A view of the complex showing the atom numbering scheme. The Ni, O and N atoms are partially shaded. H atoms are not shown for clarity.

solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 1,2-diaminobenzene in dry ethanol. It is soluble in higher molecular weight alcohols, such as 1-butanol, but is not stable to extended reflux in these solvents. When refluxed in these alcohols, the compound dissociates and organic condensation products, such as 2,4-diphenyl-3H-1,5-benzodiazepine and 2-phenylbenzimidazole, are found. No evidence of any macrocycle is detected.

Since the nickel(II) complex of the tetramethyl macrocycle (**1b**) is readily formed via template condensation [7], it was of interest to determine if solutions of the bis(1,2-diaminobenzene) adduct of bis(2,4-pentanedionato)nickel(II) (**2b**) would yield macrocycle upon extended reflux. When **2b** is heated in ethanol, the solid appears to dissolve but a light blue solid forms shortly afterward. Elemental analysis of this material indicates that the diketone, Ni, and diamine are present in the ratio of 4:2:1 (see 'Experimental', compound 3). Fackler has prepared the dimeric compound, pyridine-tetrakis(2,4-pentanedionato)dinickel(II), by treating the anhydrous bis(2,4-pentanedionato)nickel(II) trimer with pyridine [11]. A similar structure is proposed for the light blue solid which can be prepared in good yield by heating **2b** in ethanol for 45 min.

TABLE IV. Formation of Macrocycle **1b** by Reflux of Compound **2b**

Solvent	Ni(II) added	Macrocycle yield (%)	3 yield (%)
Ethanol (72 h)	1 equivalent	1.2	39.7
1-Butanol (72 h)	0	0.15	80.0
1-Butanol (24 h)	1 equivalent	6.93	0

When solutions of compound **2b** were refluxed under different conditions to try to optimize macrocycle formation, the two products isolated were the tetramethyl macrocycle (**1b**) and compound 3. The results are summarized in Table IV. In each case, the adduct appeared to dissolve and a solid then precipitated within a few minutes indicating the formation of 3. When compound **2b** and an equimolar amount of nickel acetate were refluxed in ethanol, a small yield of macrocycle (1%) was observed. This indicates that some molecules of compound 3 are dissociating and that the nickel(II) ion can impede reformation of the complex thereby allowing the component pieces to react in another manner. The major product is still compound 3, but a significant amount of the open-ended macrocyclic intermediate, $[N,N'-(1,3\text{-dimethyl-1,3-propanediylidene})\text{bis}(1,2\text{-benzenediaminato})-N,N',N'',N''']\text{nickel(II)}$ (**4**), was shown to be present by chromatography. This strongly suggests that macrocyclic yield can be improved by a longer reflux time because the ring closure between the intermediate and a second mole of diketone is rate-limiting [12]. Since compound **2b** was prepared using a modification of the literature procedure employed in the synthesis of the macrocyclic intermediate **4**, this adduct is also probably the light blue solid observed (but not identified) by Dolphin *et al.* [10].

Reflux of compound **2b** in a higher boiling alcohol (1-butanol) should increase the amount of dissociation but in the absence of added nickel acetate, recoordination predominates and only a trace of

macrocycle (**1b**) is observed. However, reflux of **2b** in 1-butanol with an equimolar amount of nickel acetate present causes a dramatic increase in macrocyclic yield in a shorter amount of time.

The failure of adduct **2a** to yield macrocycle under the same conditions can be attributed to the steric sensitivity of the template condensation [12, 13]. The observation of heterocyclic products after refluxing solution of the adduct indicates that it is dissociating, however, the phenyl groups of the diketone may sterically impede macrocycle formation [13].

Divalent transition metal complexes of 1,3-diketones are known to oligomerize [14]. For example, anhydrous bis(2,4-pentanedionato)nickel(II) exists as a trimer. Since the tendency towards oligomerization is reduced as the groups on the diketone become bulkier, a dimeric complex similar to compound **3** is not observed when solutions of adduct **2a** are refluxed.

The infrared spectrum of **2a** shows absorbances attributable to the N–H stretch of both the uncoordinated (3390, 3350 cm^{-1} , sharp) and coordinated (3290, 3230 cm^{-1} , broad) primary amine groups. The assignment of the coordinated N–H stretch is based on the observation of Marcotrigiano *et al.* that the N–H stretching frequency of an amine is lowered by 100–200 cm^{-1} when coordinated to a nickel(II) 1,3-diketone [15]. Upon washing with CH_3OD , the N–H bands disappear and the N–D stretches appear at 2530, 2500, 2390 and 2370 cm^{-1} .

The most convincing piece of evidence against the reported synthesis of the iron(III) complex of **1a** was that the absorbance at 1670 cm^{-1} (thought to be C=N stretch) disappeared upon washing with CH_3OD [6]. This result indicated that this peak was an N–H band and the iron(III) compound was assigned a structure analogous to adduct **2a**. Like its iron(III) analog, the spectrum of **2a** shows bands at 1635 and 1615 cm^{-1} that vanish upon deuteration. The infrared spectrum of compound **2b** shows similar stretching and banding modes that also vanish upon treatment with deuterated alcohol.

Bis-adducts of bis(1,3-diphenyl-1,3-propanedionato)nickel(II) are known for several nitrogenous bases such as piperidine, morpholine, and 3-methylpyridine [15, 16]. Direct structural comparison of these adducts or parent nickel(II) 1,3-diketone to adduct **2a** are not possible since the structures have not been reported. The structures of the Cu(II) and Pd(II) complexes of 1,3-diphenyl-1,3-propanedione are known [17, 18].

The C–C bonds of the planar six-membered nickel(II) diketone chelate are of equal lengths as are the C–O bonds of this ring. The C–C and C–O bond lengths indicate delocalization of the double bonds which is consistent with the aromatic character typically ascribed to metal 1,3-diketones [19].

The planes of the diketone phenyl rings are rotated 32.9° and 44.8° relative to the six-membered chelate ring. The phenyl rings of the copper(II) diketone are rotated 6.5° and 11° [17] and those of the palladium(II) chelate 5.5° and 8.5° [18]. The comparatively large rotation in adduct **2a** may be attributable to the axial coordination of the bulky diamine and are a good indication of the steric problems encountered in attempting to convert this compound to macrocycle.

The diamino ligand is axially coordinated with a Ni–C–N bond angle of 118.2°. The carbon atoms of the diamino phenyl rings are planar and since the dihedral angle between this plane and the plane containing these carbon atoms and the diamino nitrogens is only 1.8°, the diamino ligand is being considered to be planar.

The planes of the diamino ligand and the nickel chelate are not parallel, rather there is a dihedral angle of 28.2°. Another indication of potential steric problems is the fact that one of the diketone phenyl rings (C10–C15) is rotated 42.5° relative to the diamino ligand. The other diketone phenyl ring (C4–C9) is rotated only 10.5°.

The overall pseudo-octahedral geometry is common to adducts of metal 1,3-diketones and has been observed in several examples such as bis(2,4-pentanedionato)nickel(II) dihydrate, bis(2,4-pentanedionato)nickel(II)bis(pyridine), and the analogous cobalt(II) complexes [13].

The attempted preparation of the sterically crowded macrocycle, 6,8,15,17-tetraphenyldibenzo-[b,i][1,4,8,11]tetraazacyclotetradecine, via a template condensation results in the isolation of the bis-(1,2-diaminobenzene) adduct of bis(1,3-diphenyl-1,3-propanedionato)nickel(II). Extended reflux of this adduct does not induce macrocycle formation and the crystal structure illustrates the steric problems that might be encountered during macrocycle formation.

When solutions of bis(2,4-pentanedionato)nickel(II)bis(1,2-diaminobenzene) (**2b**) were refluxed under different conditions, the macrocyclic yield varied greatly. Although the yield was greatest in refluxing 1-butanol, the standard literature procedures use ethanol or methanol [7, 12]. However, in order to achieve a reasonable yield using 1-butanol, it was necessary to add nickel acetate to the reaction mixture. It appears that the added nickel(II) is necessary to prevent oligomerization of the nickel(II) 1,3-diketone once the labile diamino ligands have dissociated. The macrocyclic yield is therefore enhanced if the formation of the dimeric compound, (1,2-diaminobenzene)tetrakis(2,4-pentanedionato)nickel(II), is minimized.

Bis(1,2-diaminobenzene) adducts of nickel(II) 1,3-diketones are not macrocyclic intermediates but rather competing products and they do not

provide an attractive alternative route to dibenzotetraaza[14]annulene macrocycles. Little or no adduct formation is observed in the literature procedures employed in macrocycle preparation [7, 8] and any that is observed dissociates and the component pieces react together or with other species present. Adduct formation should be observed in situations where the condensation reaction is slow or, as in the case of 1,3-diphenyl-1,3-propanedione, completely hindered.

Supplementary Material

Anisotropic temperature factors for non-hydrogen atoms (Table S-1), hydrogen atom coordinates (Table S-2) and the structure factor table (Table S-3) have been deposited with the Editor-in-Chief.

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