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Effect of the β -diketonate ligand on the spin states of [Ni(β -dkt)₂(NH₂-quin)] complexes

Darunee Sertphon^a, David J. Harding^{a,*}, Phimphaka Harding^a, Harry Adams^b

^a Molecular Technology Research Unit, School of Science, Walailak University, Thasala, Nakhon Si Thammarat 80161, Thailand ^b Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK

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ABSTRACT

Three new complexes [Ni(β -dkt)₂(NH₂-quin)] { β -dkt = 2,2,6,6-tetramethylheptane-3,3-dionate (tmhd) **1**, hexafluoroacetylacetonate (hfac) **2**, 1,3-diphenylpropanedionate (dbm) **3**} have been prepared by reacting [Ni(β -dkt)₂(H₂O)₂] with 8-aminoquinoline (NH₂-quin). [Ni(tmhd)₂(NH₂-quin)] is found to be solvato-chromic exhibiting a square planar geometry in CH₂Cl₂, acetone, and acetonitrile with the tmhd ligand acting unusually as a counteranion while in THF and DMSO the complex is octahedral. In contrast, **2** and **3** are octahedral in all solvents. Single crystal X-ray diffraction studies reveal octahedral nickel centres with a *cis* arrangement of the β -diketonates. The molecular packing consists of hydrogen bonded dimers which in the case of **2** and **3** are connected to one another via π ... π and C-H... π interactions, respectively. Cyclic voltammetry shows **1** and **3** oxidise irreversibly at 0.46 and 1.17 V, respectively.

1. Introduction

The control of spin states remains a considerable challenge in chemistry and is important because of the potential application that such compounds may have as molecular switches and devices [1-3]. In the case of Ni(II), square planar complexes have an *S* = 0 spin state while octahedral complexes have an S = 1 spin state. Thus, a change in spin state can be affected simply by coordination of additional ligands to the square planar complex [4,5]. Of particular relevance to this paper is the $[Ni(\beta-dkt)(N-N)]^+$ $(\beta-dkt = \beta-diketonate, N-$ N = bulky diamine) series prepared by Fukuda and co-workers who found the use of a bulky diamine allowed isolation of the square planar species [6–8], previously known only with diphosphines $[Ni(\beta-dkt)(P-P)]^+$ [9], while at the same time permitting access to the octahedral complex in donor solvents. Tanaka and co-workers have also reported square planar complexes $[Ni(Py(Bz)_2)(tmhd)]PF_6$ $\{Py(Bz)_2 = N, N-bis(benzyl) - N-[(2-pyridyl)methyl]amine;$ tmhd =2,2,6,6-tetramethyl-heptane-3,5-dionate} this time with a tertiary amine-imine ligand [10]. In both instances, the complexes exhibit solvatochromism and thermochromism. While the physical properties of these compounds have been well studied the redox chemistry of these systems and the effect this may have on the change in spin states is poorly understood [11,12]. In this paper we explore a new series $[Ni(\beta-dkt)_2(NH_2-quin)]$ (NH₂-quin = 8-aminoquinoline), in which unusually $[Ni(tmhd)_2(NH_2-quin)]$ is high spin (S = 1) in the solid state and either high spin or low spin (S = 0) in solution depending on the solvent.

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2. Results and discussion

2.1. Synthesis and IR spectroscopic studies of $[Ni(\beta-dkt)_2(NH_2-quin)]$

The addition of NH₂-quin to a solution of $[Ni(\beta-dkt)_2(H_2O)_2]$ yields the expected $[Ni(\beta-dkt)_2(NH_2-quin)]$ { β -dkt = 2,2,6,6-tetramethylheptane-3,3-dionate (tmhd) **1**, hexafluoroacetylacetonate (hfac) **2**, 1,3-diphenylpropanedionate (dbm) **3**} complexes in moderate to excellent yield as blue-green or green solids (Scheme 1 and Table 1). Interestingly, while all the solids are green the reaction mixture in the case of **1** was red-purple suggesting that complex in solution and that in the solid state were different a fact later confirmed by UV–Vis spectroscopy (*vide infra*). IR spectroscopy reveals an NH stretch between 3286 and 3436 cm⁻¹ consistent with the presence of a coordinated amino group from the NH₂-quin ligand. Further bands between 1645 and 1582 cm⁻¹ are typical of chelating β -diketonate ligands with the position dependent on the substituent groups on the β -diketonate ligand and similar to those reported for $[Ni(\beta-dkt)_2(N-N)]$ (N–N = diamine, diimine) [11–13].

2.2. Electronic spectra of $[Ni(\beta-dkt)_2(NH_2-quin)]$ **1–3** in coordinating and non-coordinating solvents

The unusual colour of the reaction mixture for **1** led us to investigate the electronic spectra of **1–3** in a variety of different solvents (Table 2). In the case of **2** and **3** there are low intensity peaks above



^{*} Corresponding author. Tel.: +66 75 672094; fax: +66 75 672004. E-mail address: hdavid@wu.ac.th (D.J. Harding).

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Scheme 1. Synthesis of [Ni(β-dkt)₂(NH₂-quin)] 1–3.

Table 1	
Physical and IR spectroscopic data for $[Ni(\beta-dkt)_2(NH_2-quin)]$ 1–3.	

Compound	l Yield (%)	Colour	$IR (cm^{-1})^a$			
			v _{NH}	v _{co}	v _{CN}	
[Ni(tmhd) ₂ (NH ₂ - quin)] 1	34	Green	3339(m)	1582(s)	1420(s)	
[Ni(hfac) ₂ (NH ₂ -quin)] 2	80	Blue- green	3286(m)	1645(s)	1489(s)	
[Ni(dbm) ₂ (NH ₂ - quin)] 3	66	Green	3436(m)	1595(s)	1478(s)	

^a In KBr.

Table 2UV-Vis spectroscopic data of 1-3.

Complex	Solvent	$\lambda_{\rm max}/{\rm nm}$ (ε)
1	CH_2Cl_2	254 (38 040), 276 (26 080), 315 (4380), 332 (3190),
		528 (860), 671sh (170)
	Acetone	525 (570), 665 (100)
	Acetonitrile	526 (632), 653 (101)
	THF	505 (80), 634 (60)
	DMSO	511 (80), 676 (70)
2	CH_2Cl_2	351 (22 400), 616 (12), 672 (6), 797 (4)
3	CH_2Cl_2	252 (45 850), 340 (51 970), 672 (15)

600 nm in all solvents typical of d–d transitions for octahedral nickel complexes. The band at 672 nm is assigned to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ transition by comparison with [Ni(Py(Bz)₂)(tmhd)]PF₆ [10]. In contrast, **1** clearly exhibits solvatochromism. Thus, in CH₂Cl₂, acetone and acetonitrile the solution is red-purple and there is an intense band between 525 and 528 nm consistent with a four-coordinate square planar nickel centre and assigned to a ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition [14]. However, in strong donor solvents such as DMSO or THF the solution becomes green and bands at 550 and 672 nm are observed indicative of an octahedral nickel centre suggesting coordination of the solvent molecules (Fig. 1). Interestingly, solvatochromic Ni(II) complexes typically require non-coordinating anions such as BPh₄ or PF₆ and when coordinating anions such as nitrate are present the complex is invariably six coordinate [6-8,10]. In this system the second tmhd ligand acts as a counteranion in all complexes and is to the best of our knowledge unprecedented. It is possible that the larger tmhd ligand is better able to stabilize the four coordinate complex compared with the hfac and dbm ligands, although electronic effects may also be important as the hfac and dbm ligands would be expected to make the nickel centre more electron poor thus favouring an octahedral geometry.

2.3. Structural studies of $[Ni(\beta-dkt)_2(NH_2-quin)]$ 1-3

Crystals of **1** were grown by slow evaporation of CH_2Cl_2 /hexane solution while those of **2** and **3** were grown by allowing a solution of the complex in CH_2Cl_2 to diffuse into hexane. The structure of **1** is shown in Fig. 2 as a representative example while selected bond lengths and angles are given in Table 3. It should noted that the structure of **1** contains two independent molecules in the asymmetric unit while that of **3** contains CH_2Cl_2 as a solvent of crystallization. The structures are all broadly similar with an octahedrally coordinated Ni centre and *cis*-coordinated β -diketonate ligands



Fig. 1. UV-Vis spectra of [Ni(tmhd)₂(NH₂-quin)] 1 in CH₂Cl₂, MeCN, acetone, THF and DMSO.



Fig. 2. POVRAY diagram of $[Ni(tmhd)_2(NH_2-quin)]$ **1**, drawn with 50% ellipsoids. Only one of the independent molecules and the amino hydrogens are shown for clarity.

Table 3	
Bond lengths and angles for	[Ni(β-dkt) ₂ (NH ₂ -quin)] 1–3 (Å, °).

	1	1a	2	3
Ni-O(1)	2.021(4)	2.025(4)	2.063(14)	2.035(2)
Ni-O(2)	2.032(4)	2.023(3)	2.057(14)	2.022(2)
Ni-O(3)	2.038(4)	2.041(4)	2.053(13)	2.055(2)
Ni-O(4)	2.024(4)	1.994(4)	2.025(14)	2.041(2)
Ni-N(1)	2.122(4)	2.116(4)	2.066(16)	2.083(2)
Ni-N(2)	2.118(5)	2.134(5)	2.079(17)	2.098(2)
O(1)-Ni-O(2)	89.32(15)	90.08(15)	88.78(6)	90.54(8)
O(3)-Ni-O(4)	87.50(15)	88.61(15)	90.26(5)	88.79(8)
N(1)-Ni-N(2)	79.20(17)	77.84(16)	81.08(7)	80.58(9)
β	22.33	7.11	1.44	22.79
	13.51	25.18	6.80	13.24

enforced by the chelating NH₂-quin ligand. The Ni–O bond lengths vary from 1.994 to 2.063 Å with **1** exhibiting *on average* the shortest bonds despite the tmhd ligand having the largest steric bulk. In contrast, the Ni–N bond lengths are shortest for **2** and longest for **1** with the difference between the average Ni–N bond lengths ca. 0.05 Å. The difference is probably due to the more electron withdrawing CF₃ groups of the hfac ligand which makes the metal centre more electron poor and hence shortens the Ni–N bond. Similar Ni–O and Ni–N bond lengths are found in [Ni(Py(Bz)₂)(tmhd)(-NO₃)] [10]. In the case of **1** and **3**, the nickel centre lies slightly above the plane of one of the β -diketonate ligand exhibits a 'planar' coordination mode [11,12]. A similar 'planar' coordination mode is found for both hfac ligand.

There are two sets of N–H…O interactions between the amino protons of the NH₂-quin ligand and the coordinated O atoms of the β -diketonate forming discrete dimers (Fig. 3). Similar interactions are also found in [Ni(dbm)₂(dmae)] (dmae = dimethylamino-ethylamine) and appear to be a feature of these types of compounds [11]. Interestingly, in **1** the H-bonds are virtually identical differing by only 0.01 Å, while in **2** and **3** the difference is 0.43–0.49 Å (Table S1). The reason for this striking difference is unclear. In addition to H-bonding interactions, the structure of **2** also has $\pi \cdots \pi$



Fig. 3. POVRAY diagram of $[\rm Ni(hfac)_2(\rm NH_2-quin)]$ 2 showing the $\rm NH\cdots O$ hydrogen bonds.



Fig. 4. POVRAY diagram of $[Ni(hfac)_2(NH_2-quin)]$ **2** showing the $\pi \cdots \pi$ interactions. Symmetry code: (i) -x, 1 - y, 1 - z.

interactions in which one of the aromatic rings of the NH₂-quin ligand overlaps with its neighbour {Cg $1 \cdots$ Cg $1^* = 3.521(4)$ Å where Cg1 is the centroid of C11 \rightarrow C15,N1 and * = symmetry code = -x, 1 - y, 1 - z; see Fig. 4}. The combination of this with the H-bonding interaction results in formation of a 1D chain. However, in the structure of **3** this interaction is replaced by two C-H $\cdots \pi$ interactions between a hydrogen atom on the NH₂-quin ligand and the aromatic rings of the dbm phenyl group thereby forming a square {C3-H $3\cdots\pi$ (C19 \rightarrow C24) 2.587 Å, see Fig. 5}. This change in the type of interaction may be due to the larger bulk of the dbm ligand compared with the hfac ligand.

2.4. Electrochemical studies of $[Ni(\beta-dkt)_2(NH_2-quin)]$ 1–3

The complexes **1–3** have been studied by cyclic voltammetry (CV) in dry CH_2Cl_2 under inert conditions and reveal irreversible one-electron oxidation for complexes **1** and **3** while in the case of **2** there is no oxidation observed within the solvent window. The CVs of [Ni(tmhd)(NH₂-quin)][tmhd] **1** and [Ni(dbm)₂(NH₂-quin)] **3** are shown in Fig. 6. The cyclic voltammogram of the *dbm* complex **3** is similar to that of other [Ni(dbm)₂(N–N)] (N–N = phen and bipy) complexes with an oxidation potential of 1.17 V. Although the previously reported [Ni(tmhd)₂(N–N)] (N–N = diimine ligands) complexes exhibit reversible oxidation waves



Fig. 5. POVRAY diagram of [Ni(dbm)₂(NH₂-quin)] **3** showing the C-H $\cdots\pi$ interactions. Symmetry code: (i) -1 - x, 2 - y, 1 - z.



Fig. 6. Cyclic voltammogram of [Ni(tmhd)(NH₂-quin)][tmhd] 1 and [Ni(dbm)₂(NH₂-quin)] 3 at scan rate 100 mV/s.

at ca. 0.85 V the oxidation potential for the *tmhd* complex **1** is much lower at 0.46 V and *irreversible* consistent with the square planar geometry of complex **1** in an inert solvent such as CH_2CI_2 [11,12]. As noted in the introduction the lack of other redox studies on such systems makes further comparison difficult.

3. Experimental

3.1. Materials

All reactions were conducted in air using HPLC grade solvents. $[Ni(tmhd)_2(H_2O)_2]$, $[Ni(hfac)_2(H_2O)_2]$ and $[Ni(dbm)_2(H_2O)_2]$ were

prepared by literature methods [15,16]. All other chemicals were purchased from Fluka Chemical Company and used as received. Elemental analyses and ESI-MS were carried out by the staff of the School of Chemistry, University of Bristol, UK. Elemental analyses were carried out on a Eurovector EA3000 analyser. ESI-MS were carried out on a Bruker Daltonics 7.0T Apex 4 FTICR Mass Spectrometer.

3.2. Spectroscopy

Infrared spectra, as KBr discs, were recorded on a Perkin-Elmer Spectrum One infrared spectrophotometer in the range 400–4000 cm⁻¹. Electronic spectra were recorded in HPLC grade solvents on a Shimidzu UV1700 UV–Vis spectrometer between 200 and 900 nm.

3.3. X-ray crystallography

Crystal data and data processing parameters for the structures of **1**, **2** and **3** are given in Tables 3 and 4. X-ray quality crystals of 2 and 3 were grown by allowing hexane to diffuse into a concentrated solution of the complex in CH_2Cl_2 while those of **1** were grown by slow evaporation of solution of **1** in CH₂Cl₂/hexane. Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 100 K in a stream of cold nitrogen. All diffraction data were collected on a Bruker APEX II area detector with graphite monochromated Mo K α (λ = 0.71073 Å). After data collection, in each case an empirical absorption correction (sadabs) was applied [17] and the structures were then solved by direct methods and refined on all F^2 data using the SHELX suite of programs [18]. In all cases non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters which were ca. 1.2 \times (aromatic CH) or 1.5 \times (Me) the equivalent isotropic thermal parameters of their parent carbon atoms. In the structure of 1 the CH₂Cl₂ molecule was disordered and this was modelled by splitting the molecule into two parts. Similar disorder was found in some of the CF_3 groups of 2 which were also modelled over two positions. X-SEED was used as a graphical interface with SHELX and pictures were generated using POV-Ray [19,20].

3.4. Electrochemistry

Electrochemical studies were carried out using a palmsensPC Vs 2.11 potentiostat in conjunction with a three electrode cell. The auxiliary electrode was a platinum rod and the working electrode was a platinum disc (2.0 mm diameter). The reference electrode was a Ag–AgCl electrode. Solutions were 5×10^{-4} M in the test compound and 0.1 M in [NBuⁿ₄][PF₆] as the supporting electrolyte. Under these conditions, $E^{o'}$ for the one-electron oxidation of [Fe(η -C₅H₅)₂] added to the test solutions as an internal calibrant is 0.52 V.

Table 4

			-			
Cructallographic	data and	ctructure	rofinomont	for	complayor	1 2
		suuciure	rennement	IOI	complexes	1-2.

Complex	1 tmhd	2 hfac	3 dbm
Chemical formula Formula weight	C ₃₁ H ₄₆ N ₂ NiO ₄ 569.41	$C_{19}H_{10}F_{12}N_2NiO_4$ 617.00	C ₄₀ H ₃₂ C ₁₂ N ₂ NiO ₄ 734.29
Crystal system	triclinic	triclinic	triclinic
Space group	$P\overline{1}$	P1	P1
a (Å)	12.0928(13)	9.7729(2)	11.083(3)
b (Å)	14.8973(17)	10.2521(2)	11.273(3)
<i>c</i> (Å)	19.744(2)	12.3288(3)	15.259(4)
α (°)	69.521(6)	113.2910(10)	88.488(14)
β (°)	87.000(6)	91.5050(10	70.406(12)
γ (°)	69.481(5)	95.1900(10)	77.383(13)
V (Å ³)	3110.6(6)	1127.34(4)	1750.4(8)
Ζ	2	2	2
D_{calc} (g cm ⁻³)	1.216	1.818	1.393
μ (Mo K $lpha$) (mm $^{-1}$)	0.659	0.990	0.751
T (K)	150(2)	293(2)	293(2)
Reflections collected	43 823	19 933	15 283
Independent reflections, (R _{int})	13 878, 0.091	5206, 0.0139	7992, 0.036
$R_1, wR_2 [I > 2\sigma(I)]$	0.0787, 0.2252	0.0363, 0.0909	0.0550, 0.1354
R_1 , wR_2 (all data)	0.1716, 0.2925	0.0395, 0.0939	0.0776, 0.1503

3.5. Synthesis of [Ni(tmhd)₂(NH₂-quin)] 1

To a pale purple solution of $[Ni(tmhd)_2(H_2O)_2]$ (0.9338 g, 2 mmol) in CH₂Cl₂ (10 cm³) was added 8-aminoquinoline (0.2884 g, 2 mmol). After stirring for 2 h the red-purple solution was evaporated to low volume (ca. 2 cm³) and then hexane (15 cm³) was added. The mixture was allowed to evaporate slowly to yield green crystals 0.3911 g (34%). $v_{max}(KBr)/cm^{-1}$ 3339 (v_{NH}), 1582 (v_{CO}), 1420 ($v_{C=N}$). UV–Vis $\lambda_{max}(CH_2Cl_2)/nm$ (ε , dm³ mol⁻¹ cm⁻¹) 254 (38 040), 276 (26 080), 315 (4380), 332 (3190), 528 (860), 671sh (170). *m/z* (ESI) 385 [M–tmhd]⁺. Anal. Calc. for C₃₁H₄₆N₂O₄Ni: C, 65.39; H, 8.14; N, 4.92. Found: C, 65.22; H, 8.11; N, 4.69%.

3.6. Synthesis of [Ni(hfac)₂(NH₂-quin)] 2

To a blue-green solution of $[Ni(hfac)_2(H_2O)_2]$ (0.2574 g, 0.5 mmol) in CH_2Cl_2 (10 cm³) was added 8-aminoquinoline (0.0721 g, 0.5 mmol). After stirring for 2 h the deep blue-green solution was evaporated to low volume (ca. 2 cm³) before hexane (5 cm³) was added giving a green precipitate. The green solid was filtered then washed with hexane (2 × 3 cm³) and air dried to yield a blue-green microcrystals 0.248 g (80%). X-ray quality crystals were grown by layering a CH₂Cl₂ solution with hexane (10 cm³) leading to blue-green crystals after 2 days. $v_{max}(KBr)/cm^{-1}$ 3286 (v_{NH}), 1645 (v_{CO}), 1489 ($v_{C=N}$). UV–Vis $\lambda_{max}(CH_2Cl_2)/m$ (ε , dm³ mol⁻¹ cm⁻¹) 351 (22 400), 616 (12), 672 (6), 797 (4). m/z (ESI) 409 [M–hfac]⁺. Anal. Calc. for C₁₉H₁₀N₂O₄F₁₂Ni: C, 36.99; H, 1.63; N, 4.54. Found: C, 36.72; H, 1.54; N, 4.55%.

3.7. Synthesis of [Ni(dbm)₂(NH₂-quin)].CH₂Cl₂ 3

Synthesized using the procedure of **2**, dark green crystals recrystallized from CH₂Cl₂/hexane, 66% yield. v_{max} (KBr)/cm⁻¹ 3436 (v_{NH}), 1595 (v_{CO}), 1478 ($v_{C=N}$). UV–Vis λ_{max} (CH₂Cl₂)/nm (ε , dm³ mol⁻¹ cm⁻¹) 252 (45 850), 340 (51 970), 672 (15). *m/z* (ESI) 449 [M–CH₂Cl₂–dbm]⁺. *Anal.* Calc. for C₄₀H₃₂N₂O₄Cl₂Ni: C, 65.43; H, 4.93; N, 3.82. Found: C, 65.67; H, 4.84; N, 3.99%.

4. Conclusions

In conclusion, we have successfully prepared three novel [Ni(β -dkt)₂(NH₂-quin)] complexes which while exhibiting the same octahedral geometry in the solid state, in solution the geometry depends principally upon the type of β -diketonate and in the case of tmhd on the nature of the solvent. The wide variety of β -diketonate ligands available combined with an easily modifiable aminoquinoline framework makes this a promising system for further study in the development of molecular switches.

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Appendix A. Supplementary data

CCDC 838299, 838300 and 838301 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.08.014.

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