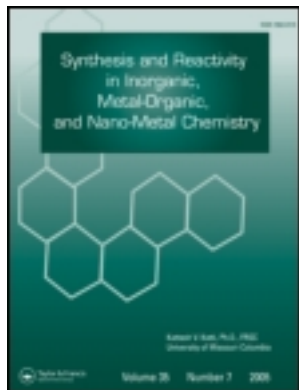


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Synthesis and Physicochemical Studies of Nickel(II) Complexes of 2-substituted-1,3-diphenyl-1,3-propanedione, their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts and X-Ray Structure of (2,2'-Bipyridine)Bis(1,3-diphenyl-1,3-propanedionato) Nickel(II)

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Synthesis and Physicochemical Studies of Nickel(II) Complexes of 2-substituted-1,3-diphenyl-1,3-propanedione, their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts and X-Ray Structure of (2,2'-Bipyridine)Bis(1,3-diphenyl-1,3-propanedionato) Nickel(II)

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The nickel(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione and their 2,2'-bipyridine and 1,10-phenanthroline adducts have been prepared and characterized by microanalysis, conductance, magnetic and spectral measurements. The conductance data in nitromethane indicate that the compounds are non-electrolytes. The room temperature magnetic moments suggest that they are magnetically dilute compounds. The electronic spectra revealed the π_3 - π_4 bathochromic shifts, which were observed upon chelation while the infrared spectra showed the different shifts of the carbonyl frequencies. The X-ray crystallography showed that nickel ion is coordinated by two units of 1,3-diphenyl-1,3-propanedione and a unit of bipyridine giving it a six coordinate octahedral geometry.

Keywords conductance, diketones, magnetic, spectra, X-ray

INTRODUCTION

β -diketones and their metal complexes have been widely studied since they have remarkable application in metal extractions,^[1] as catalysts^[2–9] and as precursors for chemical vapor deposition (CVD) applications.^[10–13] The use of β -diketones in drug synthesis in pharmaceutical industry is well documented.^[14]

Studies have reported nickel(II) complexes of 1,3-diphenyl-1,3-propanedione^[15,16] but there is dearth of information

on nickel(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione and their 2,2'-bipyridine and 1,10-phenanthroline adducts. Hence the need to synthesize these compounds and study the effects of the substituents on the properties of these ligands, complexes and adducts.

In continuation of our studies on β -diketones and their derivatives,^[17,18] we report the result of our investigation on the conductivity, reflectance spectra, solution spectra, infrared, magnetic susceptibility of nickel(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione (R-dbmH, where R = methyl (Me), ethyl (Et), iso-propyl (i-Pr), normal-propyl (n-Pr), and normal-butyl (n-Bu)) and their 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts. Thermal analysis and single crystal X-ray structural analysis of Ni(dbm)₂bipy were also determined.

EXPERIMENTAL

The following reagents were used: 1,3-diphenyl-1,3-propanedione or dibenzoylmethane (dbmH) (Aldrich chemicals), potassium carbonate, nickel acetate, methyl iodide, ethyl iodide, n-propyl iodide, i-propyl iodide, n-butyl iodide (Aldrich chemicals), 2,2'-bipyridine and 1,10-phenanthroline (analytical grade).

Synthesis of the Ligands

The 2-alkyl-1,3-diphenyl-1,3-propanediones were prepared as previously reported.^[19]

Synthesis of Ni(dbm)₂·2H₂O

1,3-diphenyl-1,3-propanedione (1.44 g, 6.4 mmol) dissolved in 10 mL methanol was added to nickel(II) acetate tetrahydrate (0.80 g, 3.2 mmol) in 8 mL 40% methanol. The precipitated solids were washed with 40% methanol and dried over

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silica gel. Similar procedure was used for preparation of the other nickel(II) complexes.

Synthesis of Ni(dbm)₂bipy

The bipyridine adduct of Ni(dbm)₂.2H₂O was prepared by mixing Ni(dbm)₂.2H₂O (0.50 g, 0.99 mmol) and bipyridine (0.51 g 3.30 mmol) prior to dissolution. The mixture was dissolved in 20 mL chloroform while stirring and heating at 70°C. This continued for 5 minutes, after which 10–15 mL acetone was added to aid precipitation. The precipitates obtained were filtered, washed with few drops of acetone and dried in vacuo. Similar procedure was used for preparation of the other bipyridine and phenanthroline adducts. A single crystal of Ni(dbm)₂bipy for x-ray analysis was obtained by dissolving the precipitate in hot acetonitrile and left in the open.

Physical Measurements

Elemental analyses for C, H and N were determined by the analytical laboratory of Geological Survey of Ethiopia while the percent nickel in the compounds was determined titrimetrically with EDTA.^[20] The analytical and physical data are presented in Tables 1 and 2. The room temperature magnetic susceptibilities of the compounds were measured by MSB-AUTO (Sherwood Scientific). The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using digital conductivity meter (Labtech). The solution spectra of the compounds in methanol, ethanol and chloroform were recorded

on a Unicam UV-visible spectrophotometer using 1 cm glass cell. The reflectance spectra of the nickel(II) complexes were recorded on a Perkin Elmer Lambda 950 UV/VIS spectrophotometer at the Department of Chemical Engineering, Faculty of Technology, Addis Ababa University, Ethiopia using calcium carbonate as reference. The infrared spectra of the compounds as pressed KBr disc were recorded on Perkin Elmer spectrophotometer BX FT-IR.

Experimental Details and Crystal Data for Ni(dbm)₂bipy

Crystal data, data collection and refinement parameters are given in Table 3. Suitable crystals of C₄₀H₃₀N₂NiO₄ (2, 2'-bipyridine) bis(1,3-diphenyl-1,3-propanedionato)nickel(II) were selected at the microscope and mounted on a glass fiber. X-ray data were collected at 293 K on colorless prismatic crystals using a Nonius Kappa CCD area detector diffractometer, with Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$), in ϕ and ω scans mode.

The structure was solved within the orthorhombic space group *Pbcn* by the direct method procedure of SIR97,^[21] and refined by full-matrix least-squares technique based on F^2 , SHELXL-97.^[22] Adsorption correction: SADABS.^[23] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed geometrically and refined with isotropic displacement parameter 1.2 times greater of the attached carbon.

Pertinent crystallographic data are given in Table 3; atomic coordinates ($\times 10^4$) and equivalent isotropic displacement

TABLE 1
Analytical and physical data of Nickel(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione and their adducts

Formula	MM	Color	M.Pt (°C)	Yield (%)	μ_{eff} (B.M.)
Ni(dbm) ₂ 2H ₂ O	541.25	L.green	254–257	79	3.11
Ni(dbm) ₂ bipy ₂	817.59	Y.green	238–240	50	3.45
Ni(dbm) ₂ bipy	661.4	Y.green	258–260	68	3.00
Ni(dbm) ₂ Phen ₂	865.61	D.green	253–255	43	3.21
Ni(dbm) ₂ Phen	685.41	Green	265–267	70	3.11
Ni(Me-dbم) ₂ .2H ₂ O	569.31	Light green	262–264	49	3.16
Ni(Me-dbم) ₂ bipy ₂	845.65	Light green	97–99	55	2.66
Ni(Me-dbم) ₂ phen	713.49	Y.green	242–244	17	2.90
Ni(Et-dbم) ₂ .2H ₂ O	597.39	L.green	299–301	66	3.65
Ni(Et-dbم) ₂ bipy	717.53	Bright green	305–307	31	2.89
Ni(Et-dbم) ₂ phen	741.55	G.yellow	290–292	34	3.23
Ni(n-Pr-dbم) ₂ .2H ₂ O	625.45	Y.green	210–212	67	3.00
Ni(n-Pr-dbم) ₂ bipy	745.58	Light green	134–136	40	3.06
Ni(n-Pr-dbم) ₂ phen	769.61	D.green	165	29	3.01
Ni(i-Pr-dbم) ₂ .2H ₂ O	625.45	Y.green	189–191	85	3.00
Ni(i-Pr-dbم) ₂ bipy	745.59	Light green	124–126	41	3.03
Ni(i-Pr-dbم) ₂ phen	769.61	D.green	119–121	37	2.99
Ni(n-Bu-dbم) ₂ .2H ₂ O	653.51	G.yellow	299–301	51	3.01
Ni(n-Bu-dbم) ₂ bipy	773.65	Y.green	279–281	30	2.99
Ni(n-Bu-dbم) ₂ phen	797.67	Y.green	255–257	33	3.01

D = dark, L = lemon, Y = yellowish, G = greenish.

TABLE 2
Microanalytical data of Nickel(II) complexes of 2-substituted-1, 3-diphenyl-1, 3-propanedione and their adducts

Empirical formula		%Found				%Calculated			
		C	H	N	Metal	C	H	N	Metal
Ni(dbm) ₂ 2H ₂ O	C ₃₀ H ₂₆ O ₆ Ni	66.26	4.82	–	10.99	66.56	4.85	–	10.85
Ni(dbm) ₂ bipy ₂	C ₅₀ H ₃₈ N ₄ O ₄ Ni	73.35	4.67	6.81	6.88	73.45	4.69	6.85	7.18
Ni(dbm) ₂ bipy	C ₄₀ H ₃₀ N ₂ O ₄ Ni	72.61	4.46	4.05	8.58	72.63	4.58	4.23	8.87
Ni(dbm) ₂ Phen ₂	C ₅₄ H ₃₈ N ₄ O ₄ Ni	74.81	4.22	6.35	7.15	74.92	4.43	6.47	6.78
Ni(dbm) ₂ Phen	C ₄₂ H ₃₀ N ₂ O ₄ Ni	73.53	4.29	4.08	8.97	73.59	4.42	4.09	8.57
Ni(Me-dbm) ₂ ·2H ₂ O	C ₃₂ H ₃₀ O ₆ Ni	67.53	4.98	–	9.83	67.50	5.32	–	10.31
Ni(Me-dbm) ₂ bipy ₂	C ₄₂ H ₃₀ N ₂ O ₄ Ni	74.03	4.81	6.38	7.12	73.85	5.02	6.62	6.94
Ni(Me-dbm) ₂ phen	C ₄₄ H ₃₄ N ₂ O ₄ Ni	74.36	5.09	4.06	8.72	74.60	4.81	3.92	8.23
Ni(Et-dbm) ₂ ·2H ₂ O	C ₃₄ H ₃₄ O ₆ Ni	68.75	5.49	–	10.05	68.35	5.75	–	9.38
Ni(Et-dbm) ₂ bipy	C ₄₄ H ₃₈ N ₂ O ₄ Ni	73.90	5.63	3.59	7.95	73.65	5.35	3.90	8.18
Ni(Et-dbm) ₂ phen	C ₄₆ H ₃₈ N ₂ O ₄ Ni	74.80	4.92	3.55	8.13	74.50	5.18	3.78	7.92
Ni(n-Pr-dbm) ₂ ·2H ₂ O	C ₃₆ H ₃₈ O ₆ Ni	69.63	5.85	–	9.10	69.13	6.14	–	9.39
Ni(n-Pr-dbm) ₂ bipy	C ₄₆ H ₄₂ N ₂ O ₄ Ni	75.82	5.45	3.95	7.95	74.10	5.69	3.76	7.87
Ni(n-Pr-dbm) ₂ phen	C ₄₈ H ₄₂ N ₂ O ₄ Ni	75.14	5.59	3.42	7.23	74.91	5.51	3.64	7.63
Ni(i-Pr-dbm) ₂ ·2H ₂ O	C ₃₆ H ₃₈ O ₆ Ni	68.94	5.89	–	9.47	69.13	6.14	–	9.39
Ni(i-Pr-dbm) ₂ bipy	C ₄₆ H ₄₂ N ₂ O ₄ Ni	74.56	6.11	3.52	7.94	74.10	5.69	3.76	7.87
Ni(i-Pr-dbm) ₂ phen	C ₄₈ H ₄₂ N ₂ O ₄ Ni	75.20	5.42	3.46	7.84	74.91	5.51	3.64	7.63
Ni(n-Bu-dbm) ₂ ·2H ₂ O	C ₃₈ H ₄₂ O ₆ Ni	69.53	6.28	–	9.16	69.84	6.49	–	8.98
Ni(n-Bu-dbm) ₂ bipy	C ₄₈ H ₄₆ N ₂ O ₄ Ni	74.73	6.29	3.82	7.28	74.51	6.01	3.62	7.59
Ni(n-Bu-dbm) ₂ phen	C ₅₀ H ₄₆ N ₂ O ₄ Ni	75.59	5.98	4.03	7.15	75.28	5.82	3.51	7.36

TABLE 3
Crystallographic data for C₄₀H₃₀N₂NiO₄

Empirical formula	C ₄₀ H ₃₀ N ₂ NiO ₄
Formula weight	661.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Volume	6740(2) Å ³
Z, Calculated density	8, 1.304 Mg·m ⁻³
Absorption coefficient	0.619 mm ⁻¹
F(000)	2752
Crystal color and shape	Colorless, prism
Crystal size	0.07 × 0.03 × 0.03 mm
Limiting indices	−40 ≤ <i>h</i> ≤ 38, −9 ≤ <i>k</i> ≤ 12, −26 ≤ <i>l</i> ≤ 27
Reflections collected/unique	43643/7676 [<i>R</i> _{int} = 0.1437]
Completeness	99.2 % (<i>θ</i> = 27.51)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7676/0/432
Goodness-of-fit on <i>F</i> ²	1.026
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0768, <i>wR</i> ₂ = 0.1837
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1887, <i>wR</i> ₂ = 0.2324
Largest diff. peak and hole	0.998 and −0.292 e·Å ⁻³

parameters are reported in Table 4; selected bond lengths and angles are given in Table 5; Figure 1 depicts the asymmetric unit of the compound with the atomic numbering scheme.

The molecule adopts octahedral geometry at Ni(II) atom, with the two nitrogens of bipyridine moiety (bipy), and two couples of oxygens from different (1,3-diphenyl-1,3-propanedionato) groups being the donor atoms.

Within the bipy ligand, the narrowing of N1-Ni1-N2 angle of 77.7(2)° is mostly due to the geometrical constraints inside the chelate ring. Besides, the bipy ligand displays a quasi-perfect planar geometry of the whole moiety, expressed by: (i) the planarity of the bipy plane, defined by the dihedral angle through the external rings [N1-C1-C2-C3-C4-C5 and N2-C6-C7-C8-C9-C10] of 0.5(2)°; (ii) the low value of the dihedral angle between the chelating moiety and the coordination plane [N1-C5-C10-N2] [N1-Ni1-N2] = 0.2(2)°, which demonstrates the slight rotation of the ligand plane around the N1-N2 vectors.

The (1,3-diphenyl-1,3-propanedione) groups show internal distortion, expressed by the external phenyl rings dihedral angles [C11-C12-C13-C14-C15-C16]∧[C17-C18-C19-C20-C21-C22] = 16.2(2)° and [C26-C27-C28-C29-C30-C31]∧[C32-C33-C34-C35-C36-C37] = 7.1(3)°, probably for packing reasons.

A most interesting feature regards the crystal packing. Square-planar complexes with large aromatic ligands have

TABLE 4

Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (2,2'-bipyridine) bis(4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato)nickel(II) for non-hydrogen atoms

	X	Y	Z	U (eq)
Ni1	3973(1)	1813(1)	5407(1)	43(1)
O1	3581(1)	3010(3)	4921(2)	63(1)
O2	3994(1)	3198(3)	6107(2)	52(1)
O3	3937(1)	532(3)	4681(2)	47(1)
O4	3497(1)	815(3)	5831(2)	54(1)
N1	4537(1)	2564(4)	5030(2)	48(1)
N2	4430(1)	679(4)	5870(2)	44(1)
C1	4564(2)	3500(6)	4592(3)	67(2)
C2	4953(3)	3942(6)	4361(3)	86(2)
C3	5324(2)	3361(8)	4604(3)	90(2)
C4	5291(2)	2390(7)	5043(3)	77(2)
C5	4895(2)	1998(5)	5250(2)	53(1)
C6	4350(2)	-257(5)	6293(2)	55(1)
C7	4654(2)	-982(6)	6604(3)	76(2)
C8	5066(2)	-709(7)	6446(3)	92(2)
C9	5155(2)	261(6)	6003(3)	74(2)
C10	4830(2)	932(5)	5730(2)	49(1)
C11	4242(2)	4992(5)	7020(2)	56(1)
C12	4319(2)	5697(6)	7554(3)	73(2)
C13	4026(2)	6580(6)	7780(3)	77(2)
C14	3667(2)	6779(6)	7457(3)	79(2)
C15	3585(2)	6079(5)	6905(3)	67(2)
C16	3874(2)	5162(4)	6690(2)	46(1)
C17	3075(2)	4220(5)	4060(3)	61(2)
C18	2762(2)	4670(7)	3663(3)	86(2)
C19	2462(2)	5594(7)	3885(3)	86(2)
C20	2486(2)	6047(6)	4478(3)	70(2)
C21	2794(2)	5607(5)	4868(3)	55(1)
C22	3096(2)	4679(5)	4666(2)	46(1)
C23	3426(2)	4116(5)	5092(2)	46(1)
C24	3540(2)	4799(5)	5641(3)	48(1)
C25	3801(2)	4323(5)	6110(2)	44(1)
C26	2994(2)	-421(6)	6685(3)	65(2)
C27	2702(2)	-917(8)	7106(3)	90(2)
C28	2384(2)	-1733(7)	6908(4)	87(2)
C29	2344(2)	-2040(6)	6293(3)	71(2)
C30	2640(2)	-1568(5)	5865(3)	54(1)
C31	2972(2)	-762(5)	6061(2)	45(1)
C32	3780(2)	-188(5)	3461(2)	52(1)
C33	3802(2)	-665(6)	2866(3)	65(2)
C34	3718(2)	-1993(7)	2749(3)	75(2)
C35	3611(2)	-2809(6)	3231(3)	84(2)
C36	3576(2)	-2321(5)	3841(3)	67(2)
C37	3668(2)	-997(4)	3961(2)	41(1)
C38	3664(2)	-377(4)	4602(2)	39(1)
C39	3368(2)	-808(5)	5046(2)	47(1)
C40	3302(2)	-211(5)	5625(2)	44(1)

TABLE 5

Bond lengths [Å] and angles [deg] for (2,2'-bipyridine) bis(1,3-diphenyl-1,3-propanedionato)nickel(II)

Ni1-O1	2.011(3)
Ni1-O3	2.014(3)
Ni1-O4	2.019(3)
Ni1-O2	2.038(3)
Ni1-N2	2.084(4)
Ni1-N1	2.096(4)
O1-C23	1.261(5)
O2-C25	1.276(5)
O3-C38	1.263(5)
O4-C40	1.272(5)
C23-C24	1.404(7)
C24-C25	1.385(7)
C38-C39	1.399(6)
C39-C40	1.390(7)
O1-Ni1-O3	86.70(14)
O1-Ni1-O4	93.79(16)
O3-Ni1-O4	89.57(13)
O1-Ni1-O2	89.89(13)
O3-Ni1-O2	176.47(13)
O4-Ni1-O2	91.59(14)
O1-Ni1-N2	174.16(16)
O3-Ni1-N2	93.52(14)
O4-Ni1-N2	92.05(15)
O2-Ni1-N2	89.78(14)
O1-Ni1-N1	96.44(17)
O3-Ni1-N1	88.66(14)
O4-Ni1-N1	169.49(15)
O2-Ni1-N1	90.80(15)
N2-Ni1-N1	77.73(16)

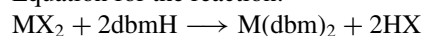
a tendency to give, in the solid state, intermolecular stacking interactions, as observed for 2,2'-bipyridine^[24] and 1,10-phenanthroline.^[25] In the present case, we observe the presence of chains of bipy ligands with interplanar space of ca. 3.5 Å. These values are indicative of a non negligible π -stacking interactions, with lowest value expressed by C2...C2^{-x+1,-y+1,-z+1} = 3.464(9) Å (van der Waals radius of carbon: 1.70 Å^[26]).

The crystal packing arrangement is completed by other interactions: C-H...O hydrogen bond,^[27] like C9-H9...O3^{-x+1,-y,-z+1} (H...O distance = 3.316(7) Å), C29-H29...O4^{-x+1/2,y-1/2,z} (H...O distance = 3.551(7) Å).

RESULTS AND DISCUSSION

The precipitates were readily obtained from aqueous-organic solvent in reasonable yield.

Equation for the reaction:



M = Ni, X = acetate ion

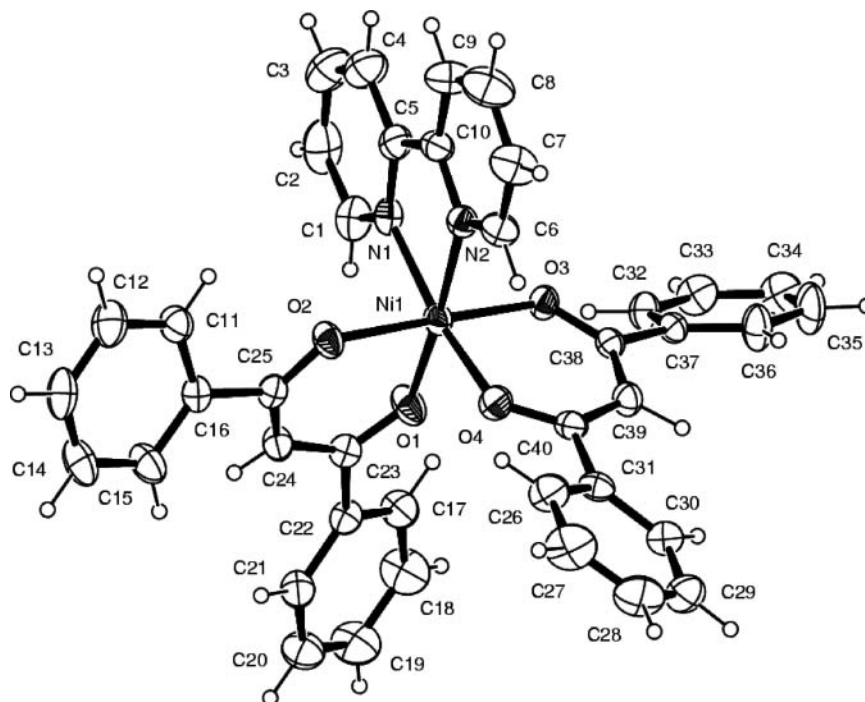


FIG. 1. The molecular structure and atomic numbering scheme for (2,2'-bipyridine)bis(1,3-diphenyl-1,3-propanedionato) nickel(II). Thermal ellipsoids are drawn at 30% probability level.

The representative equation for formation of adduct is:
 $M(\text{dbm})_2 + \text{XN-N} \longrightarrow M(\text{dbm})_2\text{N-N}_x$

(N-N = bipyridine or phenanthroline; and X = 1 or 2)

These compounds were obtained as 1:1 or 1:2 adducts

The analytical data, colors, %yields and room temperature effective magnetic moments (μ_{eff}) of the complexes are given in Tables 1 and 2. The elemental analyses are consistent with the proposed structure.

All the compounds were obtained as various shades of green except for a few that were greenish yellow in color. They exhibited poor solubility in chloroform and methanol except for a few.

The magnetic susceptibility of nickel(II) compounds at room temperature shows that they are paramagnetic with values in the range 2.66–3.65 B.M. A nickel (II) ion in an octahedral field is expected to give a spin only moment of 2.83 B.M., experimental moments of 2.9–3.3 B.M. are observed due to spin-orbit coupling of $^3A_{2g}$ and $^3T_{2g}$ (F) terms^[28] while moments of 3.2–4.1 B.M. are observed for tetrahedral nickel due to orbital contributions giving higher moments than the spin-only value of 2.83 B.M. There is no clear cut distinction between magnetic moments of tetrahedral and octahedral nickel(II) complexes, as unusual moment of 2.97 and 3.78 B.M. have been reported for tetrahedral and octahedral complexes, respectively.^[19] Ni(dbm)₂bipy₂ has a subnormal moment of 2.66 B.M, which is lower than the spin only value. The lowering of the moment observed in the compound may be attributed to interconversion of stereochemistries and/or dimerization.^[29] In the synthe-

sized complexes, lower moments were observed on substituting 2-position of Ni(dbm)₂ with alkyl groups except Ni(Me-dbm)₂·2H₂O and Ni(Et-dbm)₂·2H₂O which had increased moments. Reduction in moment may probably be due to increase in electron density around the metal leading to reduction in orbital contribution and therefore lower moment.

The molar conductivity of the compounds in nitromethane showed that they are non-electrolytes with Λ_m values of 6–29 ohm⁻¹ cm² mol⁻¹ while others have values of 33–45 ohm⁻¹ cm² mol⁻¹, which is quite high for non-electrolyte and may probably be due to appreciable partial dissociation in nitromethane.^[19] The conductance data show that the ligands are in the coordination sphere.

The selected infrared vibrational frequencies of the compounds are listed in Table 6. The infrared spectra of dbmH, Me-dbmH, Et-dbmH, n-Pr-dbmH, and n-Bu-dbmH had broad bands at 3447–3430 cm⁻¹ region which is as a result of intramolecular hydrogen bond of the enol tautomer and has been assigned to $\nu(\text{O-H})$.^[30,31] This band was not observed in the i-Pr-dbmH ligand, which could be an indication of the presence of secondary alkyl group and the absence of cis-enol tautomer because the ligand is majorly in the keto form, as previously reported.^[30,32] An appreciable coupling of different vibrational modes is usually observed in the infrared spectra of β -diketones due to overlap of absorption frequencies.^[33] In the ligand studied, the absorptions in the 1773–1598 cm⁻¹ region have been assigned as $\nu_{\text{as}}(\text{C=O}) + \nu_{\text{as}}(\text{C=C})$ vibrations^[34] while those in the 1492–1447 cm⁻¹ region have been assigned as

TABLE 6
Relevant infrared spectra bands (cm^{-1}) of 1,3-diphenyl-1,3-propanedione, the nickel(II) complexes and their adducts

Formula	C=O, C=C	$\nu_s(\text{C}-\text{O})+\delta\text{C}-\text{H}$	$\delta_{\text{as}}(\text{CH}_3) + \delta_s(\text{CH}_3)$	$\gamma(\text{C}-\text{H})$ Phen/bipy
dbmH	1598 b, 1540 b	1466b		
Ni(dbm) ₂ .2H ₂ O	1596 s, 1548 s, 1524 s	1480s		
Ni(dbm) ₂ bipy ₂	1599 s, 1552 s, 1516 s	1457w		759 m
Ni(dbm) ₂ bipy	1595 s, 1549 s, 1516 s	1457s		759 m
Ni(dbm) ₂ Phen ₂	1593 s, 1553 s, 1518 s	1479w,1456s		844 m 726 w
Ni(dbm) ₂ Phen	1595 s, 1551 s, 1516 s	1479w,1457s		843 s 726 s
Me-dbmH	1689 m, 1664 m, 1595 m	1450s	1346s	
Ni(Me-dbm) ₂ .2H ₂ O	1664 w, 1595 s, 1536 m	1478m, 1454m	1394b	
Ni(Me-dbm) ₂ bipy ₂	1691 s, 1667 m, 1595 m	1480w, 1450s	1397m	771 m
Ni(Me-dbm) ₂ phen	1595 s, 1551 s, 1517 s	1480w,1457s	1412s	847 m 723 s
Et-dbmH	1687 vs, 1665 s, 1597 vs	1466b, 1449m	1356s	
Ni(Et-dbm) ₂ .2H ₂ O	1592 s, 1530 vs	1476s, 1458s	1394b	
Ni(Et-dbm) ₂ bipy	1604 vw, 1555 vs	1471m	1397m	774 vs
Ni(Et-dbm) ₂ phen	1622 vw, 1601 vs, 1556 vs	1481m, 1462vs	1412s	845 m 722 vs
n-Pr-dbmH	1686 b, 1664 b, 1593 m	1490vw, 1453vs	1369m 1341s	
Ni(n-Pr-dbm) ₂ .2H ₂ O	1595 s, 1560 m, 1518 s	1491m, 1457s	1401b	
Ni(n-Pr-dbm) ₂ bipy	1599 s, 1567 s, 1508 s	1452s	1410s	763 s
Ni(n-Pr-dbm) ₂ phen	1652 b, 1633 b,1595 m	1481w, 1457w	1421m 1374w	846 vs 728 vs
i-Pr-dbmH	1773 w, 1689 b, 1663 b	1448vs	1339s	
Ni(i-Pr-dbm) ₂ .2H ₂ O	1600 vs,1561 vs, 1516 vs	1484vs, 1452vs	1405b	
Ni(i-Pr-dbm) ₂ bipy	1597 vs, 1506 vs	1456 m	1396b 1355vw	773 vs
Ni(i-Pr-dbm) ₂ phen	1649 b, 1628 b, 1563 s	1486w, 1457w	1423s 1403w	851 s 724 vs
n-Bu-dbmH	1693 s, 1667 s, 1596 m	1447s	1380vw 1348 m	
Ni(n-Bu-dbm) ₂ .2H ₂ O	1599 s, 1551 s, 1522 s	1478s, 1452s	1399vs	
Ni(n-Bu-dbm) ₂ bipy	1698 w, 1670 vw, 1594 s	1479w, 1457s	1418m 1399m	758 m
Ni(n-Bu-dbm) ₂ phen	1697 s, 1667 m, 1593 s	1477vw, 1457vs	1419s 1403s	845 w 721 m

b = broad, s = strong, v = very, w = weak, m = medium.

$\nu_s(\text{C}-\text{O})+\delta\text{C}-\text{H}$. The infrared band assignment of β -diketones showed that strongly electron-withdrawing substituents produce high $\nu_{\text{as}}(\text{C}=\text{O})+\nu_{\text{as}}(\text{C}=\text{C})$ while electron-releasing substituents produce low $\nu_{\text{as}}(\text{C}=\text{O})+\nu_{\text{as}}(\text{C}=\text{C})$.^[35,36] Alkyl groups have electron-releasing effects and this effect is a manifestation of the positive inductive effect. The electron-releasing effect of the alkyl groups tends to increase slightly with increasing length of the alkyl chain.^[37] A decrease was observed in the $\nu_{\text{as}}(\text{C}-\text{O})+\nu_{\text{as}}(\text{C}-\text{C})$ of 2-substituted-1,3-diphenyl-1,3-propanedione as the size of the substituent increases except Me-dbmH and i-Pr-dbmh which showed an increase in frequency. The decrease in frequency indicates the positive inductive effect of the alkyl group on the system. Single bands of $\nu_s(\text{C}-\text{O})+\delta\text{C}-\text{H}$ were observed in dbmH, Me-dbmH and i-Pr-dbmh. Et-dbmH, and n-Pr-dbmH had two distinct bands while n-Bu-dbmH had three bands. A decrease in $\nu_s(\text{C}-\text{O})+\delta\text{C}-\text{H}$ of 2-substituted-1,3-diphenyl-1,3-propanedione was observed as the length of the alkyl group increases except Et-dbmH and n-Pr-dbmH which had increased frequency. The decrease in frequency also indicates the positive inductive effect of the alkyl group on the system. A band centered around 1425 cm^{-1} is probably caused

by a methyl deformation.^[34] Similar assignment has been given by other studies in which bands at 1425 cm^{-1} in acetylacetone was assigned to a methyl deformation.^[38] The ligands, which have no methyl group, fail to absorb in the 1425 cm^{-1} region. Bands in the $1420\text{--}1350 \text{ cm}^{-1}$ have been assigned as $\delta_{\text{as}}(\text{CH}_3) + \delta_s(\text{CH}_3)$ vibrations.^[17,19,30,31,39] In the ligands studied, these bands occurred in the $1380\text{--}1339 \text{ cm}^{-1}$. The frequency of the methyl deformation band increases as the length of alkyl increases except i-Pr-dbmH which had decreased frequency. Increased frequency of this methyl deformation may probably be attributed to the positive inductive effect of the alkyl group on the system.

The infrared spectra of the nickel(II) complexes showed that the frequencies of the asymmetric C-O and C-C stretching vibrations are lowered from the free ligand^[40,41] values in the order: Ni(i-Pr-dbm)₂.2H₂O ($\Delta\nu = 173 \text{ cm}^{-1}$) > Ni(Et-dbm)₂.2H₂O ($\Delta\nu = 95 \text{ cm}^{-1}$) > Ni(n-Bu-dbm)₂.2H₂O ($\Delta\nu = 94 \text{ cm}^{-1}$) > Ni(nPr-dbm)₂.2H₂O ($\Delta\nu = 91 \text{ cm}^{-1}$) > Ni(Me-dbm)₂.2H₂O ($\Delta\nu = 25 \text{ cm}^{-1}$) > Ni(dbm)₂.2H₂O ($\Delta\nu = 2 \text{ cm}^{-1}$). The order shows that the 2-substituted Ni(II) complexes have larger lower frequency shift than the Ni(dbm)₂.2H₂O. This probably

TABLE 7
The electronic solution spectra of 2-substituted-1,3-diphenyl-1,3-propanedione nickel(II) complexes and their adducts

Empirical formula	$\pi_3\text{-}\pi_4^*(\text{cm}^{-1})$		d-d	
	CHCl_3	CH_3OH	CHCl_3	CH_3OH
dbmH	34,483(20567)	34,364(23114)		
Ni(dbm) ₂ 2H ₂ O	32,680*	34,483(10905)	17,730(95) 13,812(91)	15,723(63)
Ni(dbm) ₂ bipy ₂	33,333(41908)	34,014(?)	17,361(39) 12,887(6)	17,361(?) 14,368(?) 12,034(?)
Ni(dbm) ₂ bipy	33,333(38,704)	33,113(?)	17,544(41)	17,361(?)
Ni(dbm) ₂ Phen ₂	34,483(26,076)	34,247*	17,065(38) 12,920(12)	17,422(12) 13,158(6)
Ni(dbm) ₂ Phen	34,247*	34,247 (?)	17,241(26)	18,116(?)
Me-dbmH	34,247(5282)	–		
Ni(Me-dbm) ₂ .2H ₂ O	33,784*	–	15,385(39)	
Ni(Me-dbm) ₂ bipy ₂	–	–	–	
Ni(Me-dbm) ₂ phen	34,247*	–	12,755(9)	
Et-dbmH	32,259(20203)	34,602(6951)		
Ni(Et-dbm) ₂ .2H ₂ O	33,003*	34,555(?)	15,949(20)	15,674(?)
Ni(Et-dbm) ₂ bipy	33,557(39426)	33,445(46,087)	15,848(28) 12,870*	
Ni(Et-dbm) ₂ phen	34,722*	34,364(?)	17,241(32)	17,513(?)
n-Pr-dbmH	32,468(?)	–		
Ni(n-Pr-dbm) ₂ .2H ₂ O	34,247(?)	–	17,094(?)	
Ni(n-Pr-dbm) ₂ bipy	33,670(?)	–	14,948(?)	
Ni(n-Pr-dbm) ₂ phen	33,445(?)	–	17,212(?)	
i-Pr-dbmH	34,483*	–		
Ni(i-Pr-dbm) ₂ .2H ₂ O	34,247(?)	–	17,153(?)	
Ni(i-Pr-dbm) ₂ bipy	33,784(?)	–	14,925(?)	
Ni(i-Pr-dbm) ₂ phen	32,445(?)	–	17,241(?)	
n-Bu-dbmH	35,211(?)	35,088(?)		
Ni(n-Bu-dbm) ₂ .2H ₂ O	–	34,843(?)		15,773(?)
Ni(n-Bu-dbm) ₂ bipy	34,247(?)	33,557(?)	16,978(?)	17,889(?)
Ni(n-Bu-dbm) ₂ phen	34,483(?)	34,364(?)	16,667(?) 14,837(?) 12,610(?)	17,483(?)

(?) Compounds are partially soluble in the solvent.

*Shoulder.

indicates the positive inductive effect of the alkyl group on the system. The $\nu_{\text{as}}(\text{C}=\text{O}) + \nu_{\text{as}}(\text{C}=\text{C})$ stretching vibrations of these nickel(II) complexes were observed in the range 1664–1516 cm^{-1} while those of the bipyridine and phenanthroline adducts were observed in the range 1698–1506 cm^{-1} . A decrease in $\nu_{\text{s}}(\text{C}-\text{O}) + \delta\text{C}-\text{H}$ of nickel(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanediones was observed as the length of the alkyl group increases except Ni(n-Pr-dbm)₂.2H₂O which had increased frequency. The decrease in frequency indicates the positive inductive effect of the alkyl group on the system. Higher frequency shifts of varying magni-

tude were observed in the $\nu_{\text{as}}(\text{C}=\text{O}) + \nu_{\text{as}}(\text{C}=\text{C})$ vibrations of the adducts relative to the parent complexes except Ni(dbm)₂bipy, Ni(dbm)₂phen₂, Ni(dbm)₂phen, Ni(Me-dbm)₂phen and Ni(i-Pr-dbm)₂bipy, which had lower frequency shifts. These shifts could give an indication of the electron density on nickel(II) ion and the strength of the bonds in the adducts.^[34] The lower frequency shifts in the $\nu_{\text{as}}(\text{C}=\text{O}) + \nu_{\text{as}}(\text{C}=\text{C})$ vibrational modes of metal β -diketonate could be an indication of stronger Ni-O bonds in the chelate ring due to increased electron delocalization as a result of weaker Ni-N (base) interactions.^[19] Higher frequency shifts of $\nu_{\text{s}}(\text{C}-\text{O}) + \delta\text{C}-\text{H}$ were observed on

TABLE 8
The electronic solid reflectance spectra of
2-substituted-1,3-diphenyl-1,3-propanedione, nickel complex
and its adducts

Emperical formula	$\pi_3\text{-}\pi_4^*(\text{cm}^{-1})$	d-d
dbmH	35,211	
Ni(dbm) ₂ 2H ₂ O	35,336, 31,949	21,008, 18,939, 11,933
Ni(dbm) ₂ bipy ₂	34,722	19,194, 13,755, 12,706
Ni(dbm) ₂ bipy	35,971	19,417, 13,812, 12,723
Ni(dbm) ₂ Phen ₂	31,847	19,417, 13,680, 12,771
Ni(dbm) ₂ Phen	31,153	19,305, 13,699, 12,788
Me-dbmH	34,398	
Ni(Me-dbm) ₂ .2H ₂ O	33,113	20,877, 18,587, 12,107
Ni(Me-dbm) ₂ bipy ₂	31,646	20,790, 18,215, 11,669
Ni(Me-dbm) ₂ phen	31,847	21,142, 18,939, 13,387
Et-dbmH	35,088, 33,003	
Ni(Et-dbm) ₂ .2H ₂ O	34,722	20,534, 18,939, 12,034
Ni(Et-dbm) ₂ bipy	35,842	19,724, 13,587, 12,531
Ni(Et-dbm) ₂ phen	31,949	19,380, 13,624, 12,788
n-Bu-dbmH	35,971	
Ni(n-Bu-dbm) ₂ .2H ₂ O	35,714	20,747, 18,939, 12,005
Ni(n-Bu-dbm) ₂ bipy	35,461	19,342, 13,680, 12,706
Ni(n-Bu-dbm) ₂ phen	35,714	19,305, 13,793, 12,853

comparing the bipyridine adduct of nickel(II) 2-substituted-1,3-diphenyl-1,3-propanedione with the Ni(dbm)₂bipy except Ni(n-Pr-dbm)₂bipy and Ni(i-Pr-dbm)₂bipy, which had lower frequency shift. The magnitude of the shift of $\nu_s(\text{C O}) + \delta\text{C H}$ were observed in the order: Ni(n-Pr-dbm)₂bipy ($\Delta\nu = -5$) < Ni(i-Pr-dbm)₂bipy ($\Delta\nu = -1$) < Ni(Et-dbm)₂bipy ($\Delta\nu = +14$) < Ni(n-Bu-dbm)₂bipy ($\Delta\nu = +22$) < Ni(Me-dbm)₂bipy ($\Delta\nu = +23$). Higher frequency shifts of the phenanthroline adducts of nickel(II) 2-substituted-1,3-diphenyl-1,3-propanediones relative to Ni(dbm)₂phen were also observed except Ni(n-Bu-dbm)₂phen which had lower frequency shift. The M-N stretching vibrational modes normally occur below 300 cm⁻¹ and could not be observed due to instrument limitations. Therefore bands below 700 cm⁻¹ have been assigned to coupled M-O and M-N stretching vibrational modes.^[40,41]

The electronic solution spectra of the ligands, complexes and adducts were studied in chloroform and methanol and the assignments are presented in Table 7.

Hypsochromic shifts of the $\pi_3\text{-}\pi_4^*$ transition bands of the 2-substituted ligands relative to dbmH were observed in methanol except Me-dbmH, n-Pr-dbmH, and i-Pr-dbmH which were insoluble in methanol and could not be measured. Hypsochromic shifts of the $\pi_3\text{-}\pi_4^*$ transition bands could be attributed to the positive inductive effect of the alkyl groups leading to higher frequency shift.^[42] Hypsochromic shifts of the $\pi_3\text{-}\pi_4^*$ transition bands were also observed in the 2-substituted complexes in chloroform relative to Ni(dbm)₂.2H₂O and this could also be

attributed to the positive inductive effect of the alkyl groups. The magnitude of the hypsochromic shifts were observed in the order: Ni(n-Pr-dbm)₂.2H₂O ($\Delta\nu = 1567$ cm⁻¹) = Ni(i-Pr-dbm)₂.2H₂O ($\Delta\nu = 1567$ cm⁻¹) > Ni(Me-dbm)₂.2H₂O ($\Delta\nu = 1104$ cm⁻¹) > Ni(Et-dbm)₂.2H₂O ($\Delta\nu = 323$ cm⁻¹).

Absorptions at energies higher than 24,000 cm⁻¹ in metal(II) complexes of β -diketone is said to originate from charge transfer from β -diketone ion to the metal.^[43,44] Upon adduct formation, $\pi_3\text{-}\pi_4^*$ hypsochromic shifts were observed in chloroform solution of all the adducts except Ni(n-Pr-dbm)₂bipy, Ni(n-Pr-dbm)₂phen, Ni(i-Pr-dbm)₂bipy and Ni(i-Pr-dbm)₂phen which had bathochromic shifts. These shifts could give an indication of the electron density on nickel(II) ion and the strength of the bonds in the adducts.^[19] The bathochromic shifts could be an indication of stronger Ni-O bonds and weaker Ni-N and C-O bonds in the nickel adducts.^[19] The poor solubility of some of the compounds made it impossible to obtain their spectra. $\pi_3\text{-}\pi_4^*$ hypsochromic shifts were also observed in the 2,2'-bipyridine adducts of nickel(II) 2-substituted-1,3-diphenyl-1,3-propanediones relative to the Ni(dbm)₂bipy. This probably indicate the positive inductive effect of the alkyl substituents.

The ligand field spectra bands of the nickel compounds were typically of an octahedral geometry.^[45] The electronic reflectance spectra of ligands (Table 8) in the UV region displayed single bands between 35,971–33,003 except Et-dbmH, which had additional band in this region. The visible region of the spectra also showed that the nickel compounds are octahedral in geometry.

CONCLUSION

The X-ray structural analysis of Ni(dbm)₂bipy shows a six coordinate, octahedral geometry formed by coordination of the nickel(II) ion through four oxygen atoms of the 1,3-diphenyl-1,3-propanedione and two nitrogen atoms of the 2,2'-bipyridine. On the basis of the magnetic and spectral data of the other compounds, a probable six coordinate octahedral geometry is suggested for all the nickel compounds.

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