

## Synthesis and Characterization of Metal Complexes of Terdentate NNN Donor Ligands Derived from 2,6-Diacetylpyridine. Nickel(II) Complexes with 2,6-Diacetylpyridinebis(imines)

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*The synthesis and characterization of fourteen 1:1 and 1:2 nickel(II) complexes of some 2,6-diacetylpyridinebis(imines) are reported. The coordinating ability of these terdentate NNN donor ligands is comparable to that of terpyridine and is virtually independent of the amine substituent. The complexes  $NiX_2 \cdot L$  are pentacoordinate for  $X = Cl, Br, I$  but apparently octahedral via bridging anions for  $X = NCS, N_3$ . The 1:1 cyano derivative of the anil ligand adopts a dimeric  $[NiL_2][Ni(CN)_4]$  structure. The seven 1:2 complexes are of the type  $[NiL_2]Y_2$  ( $Y = Br, I, BF_4$ ) involving an octahedral cation.*

### Introduction

Metal complexes of a variety of potentially terdentate NNN donor ligands have been investigated by numerous workers [1, 2]. In complexes with divalent metal salts particular interest has focused on high-spin pentacoordinate complexes of the type  $MX_2(\text{ligand})$  [3] and octahedral complexes of general formula  $M(\text{ligand})_2Y_2$  ( $Y$  is a non-coordinating anion) which may have anomalous and temperature-dependent magnetic moments [4]. The most widely studied [5] of this class of ligands is 2,2',2''-terpyridine(terpy) (I), which has the trimethine structural unit. Unfortunately, modification of the terpyridine nucleus to alter the donor ability of the trimethine group is tedious [6]. Similarly, difficulties

in ligand synthesis has restricted the study of substituent effects in metal complexes of other terdentate NNN donor ligands.

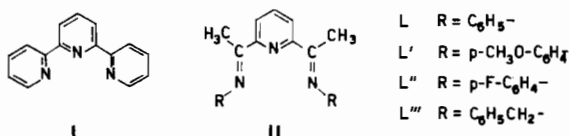
We have recently reported the high yield synthesis of a series of potentially terdentate NNN donor ligands, (II), obtained by the Schiff base condensation of 2,6-diacetylpyridine with aromatic amines [7]. In order to establish the coordinating ability and the effect of various aromatic substituents for these 2,6-diacetylpyridinebis(imines), we have prepared a number of divalent metal complexes. In the present paper, the isolation and characterization of some nickel(II) 1:1 and 1:2 complexes are reported and the results compared to those obtained by other workers for the analogous terpy complexes [8].

### Experimental

Physical measurements. Carbon, hydrogen, and nitrogen analyses were performed by Mr. S. McKinnon at the University of Guelph and by M-H-W Laboratories, Garden City, Michigan. Molecular weights were determined in nitromethane at 37 °C with a Hewlett-Packard Model 302 vapour pressure osmometer by M-H-W Laboratories. Molar conductivities were determined at approximately  $10^{-3} M$  with either an Industrial Instruments Model RC16B2 of a YSI Model 31 conductivity bridge. Magnetic and spectroscopic data were obtained as described previously [7].

Preparation of the ligands and complexes. Synthesis of the benzyl-, phenyl-, and *p*-methoxyphenyl derivatives of general formula (II) was reported earlier [7], 2,6-Diacetylpyridinebis(*p*-fluoroanil) was prepared similarly. Analytical data for the complexes are given in Table I.

Preparation of the complexes  $MCl_2 \cdot L$  and  $[ML_2](ClO_4)_2$  where  $M$  is Ni(II) and Zn(II) and  $L$  is (II)



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TABLE I. Properties and Analytical Data for the Nickel Complexes.

Compound	Colour	Decomposition Temp., °C	% Carbon	% Hydrogen	% Nitrogen
NiCl <sub>2</sub> ·L'	Brown	285–290	55.1(55.0) <sup>a</sup>	4.5(4.6) <sup>a</sup>	8.3(8.4) <sup>a</sup>
NiCl <sub>2</sub> ·L''·2H <sub>2</sub> O	Dark brown	330	49.3(49.0)	3.8(4.1)	8.2(8.2)
NiCl <sub>2</sub> ·L'''·H <sub>2</sub> O	Tan	240–245	51.1(51.6)	4.6(4.7)	7.9(7.9)
NiBr <sub>2</sub> ·L	Brown	340	47.4(47.4)	3.7(3.6)	8.0(7.9)
NiI <sub>2</sub> ·L	Red–brown	90	40.1(40.2)	3.1(3.3)	6.7(6.7)
Ni(NCS) <sub>2</sub> ·L	Light brown	290–295	56.6(56.5)	4.2(3.9)	13.6(14.3)
Ni(N <sub>3</sub> ) <sub>2</sub> ·L	Pale brown	232	55.9(55.3)	4.5(4.2)	27.9(27.7)
[NiL <sub>2</sub> ][Ni(CN) <sub>4</sub> ]	Brown	290	65.4(65.2)	4.6(4.5)	16.5(16.5)
[NiL <sub>2</sub> ]Br <sub>2</sub>	Deep brown	300–305	59.5(59.6)	4.6(4.6)	9.7(9.9)
[NiL <sub>2</sub> ]I <sub>2</sub>	Deep red–brown	305–310	53.6(53.7)	4.1(4.1)	9.5(9.0)
[NiL <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Red–brown	345	58.7(58.7)	4.3(4.5)	9.8(10.0)
[NiL' <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Red–brown	315–325	56.0(56.5)	4.7(4.7)	8.4(8.6)
[NiL'' <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Tan	330	52.9(53.1)	3.8(3.8)	8.9(8.9)
[NiL''' <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Cinnamon	285–295	60.5(60.4)	5.2(5.1)	9.0(9.2)

<sup>a</sup>Calculated percentage in parentheses.

with R = C<sub>6</sub>H<sub>5</sub> was described in the preliminary investigation [7]. Since the chloride and tetrafluoroborate derivatives of nickel(II) were readily obtained by analogous procedures for the complexes of (II) with R = *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>5</sub>-(L'), *p*-F-C<sub>6</sub>H<sub>5</sub>-(L'') and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-(L'''), only representative examples are described herein.

#### NiCl<sub>2</sub>·L'''·H<sub>2</sub>O

A 0.24 g (1.0 mmol) sample of NiCl<sub>2</sub>·6H<sub>2</sub>O and 0.34 g (1.0 mmol) of 2,6-diacetylpyridinebis(benzylimine) were added to *ca.* 20 ml absolute ethanol containing 2 ml of dimethoxypropane. After refluxing ½ hr, the solution was concentrated and benzene (180 ml) was added; further reduction of the volume and cooling gave a tan-coloured powder, which was collected on a frit, washed with benzene, and air-dried; yield, 98%.

#### [NiL'<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>

To a warm solution of 0.13 g (0.5 mmol) Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O and 0.37 g (1.0 mmol) 2,6-diacetylpyridinebis(*p*-methoxyanil) in *ca.* 25 ml ethanol was added slowly 0.24 g (2.2 mmol) NaBF<sub>4</sub> dissolved in 10 ml water. The solution was filtered hot, then cooled to give a dark red precipitate, which was collected and washed with ethanol and ether and air-dried; yield, 84%.

Since some of the NiX<sub>2</sub>·L complexes for X ≠ Cl were difficult to isolate, details of their preparation are given below.

#### NiBr<sub>2</sub>·L

To a solution of 1.0 g (3.1 mmol) NiBr<sub>2</sub>·6H<sub>2</sub>O in absolute ethanol (50 ml) was added 1.0 g (3.2

mmol) of 2,6-diacetylpyridinebis(anil). After stirring for *ca.* 3 minutes, the brown solution was filtered and reduced in volume by blowing air over the surface until crystals began to form. The brown crystalline powder that had precipitated after cooling the solution for 1 hr was collected and dried *in vacuo* at 100 °C overnight; yield, 38%.

#### NiI<sub>2</sub>·L

To a cooled solution of 1.4 g (3.3 mmol) NiI<sub>2</sub>·6H<sub>2</sub>O in absolute ethanol was added 0.5 g (1.6 mmol) of the ligand. The red–brown product that formed was immediately collected and dried *in vacuo* at room temperature; yield: 50%.

#### Ni(NCS)<sub>2</sub>·L

To a warm solution of 1.0 g (4.0 mmol) Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O in absolute ethanol containing dimethoxypropane was added 1.0 g (3.2 mmol) of the ligand. A 0.65 g (8.0 mmol) sample of NaNCS was then added to the deep red-brown solution which was refluxed for *ca.* 1 hr. Subsequent filtration and cooling gave a light green precipitate, which was recrystallized from ethanol. The product was brown after drying *in vacuo* at 100 °C; yield: 64%.

#### Ni(N<sub>3</sub>)<sub>2</sub>·L

To a dark brown solution of 1.0 g (4.0 mmol) Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O and 1.0 g (3.2 mmol) of the ligand in absolute ethanol containing dimethoxypropane was added 0.52 g (8.0 mmol) NaN<sub>3</sub>. After 2 hr reflux, a pale red–brown solid was collected, washed repeatedly with water and air-dried; yield: 75%.

TABLE II. Conductivity, Magnetic Data and Far Infrared Bands.

Compound	$\Lambda_M$ , mho $\text{cm}^2 \text{mol}^{-1}$		$\mu_{\text{eff}}$ (B.M.)	Far-Infrared Bands (400–150 $\text{cm}^{-1}$ )
	$\text{C}_2\text{H}_4\text{Cl}_2$	$\text{CH}_3\text{NO}_2$		
$\text{NiCl}_2 \cdot \text{L}'$	0.14	39	3.15	389w, 346w, 298s,b, 284sh, 238s, 196w, 178w
$\text{NiCl}_2 \cdot \text{L}'' \cdot 2\text{H}_2\text{O}$	ins.	3.2	3.29	380w, 310s
$\text{NiCl}_2 \cdot \text{L}''' \cdot \text{H}_2\text{O}$	ins.	80	3.14	334vw, 288s, 265m, 240vs, 205m, 182w, 151m.
$\text{NiBr}_2 \cdot \text{L}$	0.24	10.8	3.30	344w, 282w, 256vs, 235m, 225m, 196s, 186sh, 154w.
$\text{NiI}_2 \cdot \text{L}$	0.59	29.8	3.11	345vw, 292vw, 229sh, 221m, 207vw, 179mw.
$\text{Ni}(\text{NCS})_2 \cdot \text{L}$	ins.	7.0	3.14	347m, 292vw, 276ms, 246s, 235s, 200m,b.
$\text{Ni}(\text{N}_3)_2 \cdot \text{L}$	ins.	ins.	3.40	392w, 343m, 306 - 290s,b, 225w, 231s, 221sh, 209m, 195sh, 161w, 151m.
$[\text{NiL}_2][\text{Ni}(\text{CN})_4]$	ins.	102	2.22	394vw, 378vw, 365m, 291mw, 255sh, 242s, 218m, 204w.
$[\text{NiL}_2]\text{Br}_2$	17.9	157	3.05	240w
$[\text{NiL}_2]\text{I}_2$	17.6	210	3.16	289w, 241m, 215w.
$[\text{NiL}_2](\text{BF}_4)_2$	22.9	200	3.18	239m, 214w, 196vs
$[\text{NiL}'_2](\text{BF}_4)_2$	21.8	162	3.18	193s
$[\text{NiL}''_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$	ins.	216	3.20	377w, 215s, vb, 193s.
$[\text{NiL}'''_2](\text{BF}_4)_2$	ins.	169	3.00	213s,b, 193vs.

 $[\text{NiL}_2][\text{Ni}(\text{CN})_4]$ 

A 2.75 g (8.7 mmol) sample of the ligand was added to a warm ethanolic solution of 2.5 g (8.7 mmol)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  forming a deep brown solution immediately. A fine brown precipitate formed when 0.85 g (17 mmol) NaCN was added. The solution was filtered, taken to dryness, and the product recovered from the residue by dissolving it in nitromethane. Filtration to remove  $\text{NaNO}_3$  and cooling of the filtrate gave a dark brown solid that was recrystallized from nitromethane; yield: 25%.

## Results and Discussion

Most of the nickel(II) complexes of the ligands(II) were readily obtained by briefly refluxing ethanolic solutions of the appropriate nickel(II) salt and terdentate NNN donor ligand. The 1:2 tetrafluoroborates and the azide, cyanide, and isothiocyanate derivatives were prepared from the metal acetates or nitrates and the appropriate sodium salt. The rapid isolation of  $\text{NiX}_2 \cdot \text{L}$  (X = Br, I) was necessary to preserve the 1:1 stoichiometry. Longer reaction times, even with less than an equivalent amount of the ligand being present, led to the formation of

$[\text{NiL}_2]\text{X}_2$  or products whose analyses suggested mixtures of the 1:1 and 1:2 adducts. Such rearrangement to a bis-ligand complex was previously observed for 1:1 terpy complexes [8]. In related studies, we have isolated  $[\text{ZnL}_2](\text{NO}_3)_2$  by recrystallization of  $\text{ZnL}(\text{NO}_3)_2$  from water. We also have observed that aqueous solutions of 1:1 nickel and zinc chloride adducts of the ligands(II) show conductivities in agreement with the presence of bis-ligand cations and also that  $[\text{M}(\text{ligand})_2](\text{BF}_4)_2$  complexes may be isolated by the addition of sodium tetrafluoroborate to ethanolic solutions of 1:1 metal(II) adducts [9]. Though formation of bis-ligand complexes of the ligands(II) with aliphatic substituents was not reported in an earlier study by Sacconi and co-workers [10], it was noted that five-coordinate  $\text{NiI}_2$  complexes could not be isolated, presumably due to the steric hindrance of the bulky aliphatic groups. An alternative explanation or contributing factor to their observation might be the ready formation of  $[\text{Ni}(\text{ligand})_2]^{2+}$  species.

## The Halide Complexes

The 1:1 bromide and iodide complexes with 2,6-diacetylpyridinebis(anil) and the 1:1 chloride com-

TABLE III. Electronic Spectra of the Complexes.

Compound	State	Absorption Maxima, kK
NiCl <sub>2</sub> •L	Solid	9.1, 11.2(sh), 13.3, 19.2(sh), 26.7(sh)
NiCl <sub>2</sub> •L'	Solid	9.1(sh), 11.8, 19.2(sh), 26.3
	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	12.5, 27.8(4100).
	CH <sub>3</sub> NO <sub>2</sub>	8.3(b, 15), 11.6(29), 13.2(35), 14.1(41), 15.2(sh, 66), 27.0 (ca. 2500)
NiCl <sub>2</sub> •L''•2H <sub>2</sub> O	Solid	7.7b, 12.5, 14.3, >25.0
NiCl <sub>2</sub> •L'''•H <sub>2</sub> O	Solid	8.3, 12.8, 14.1, 15.3, 25.0(sh), >29.4
	CH <sub>2</sub> NO <sub>2</sub>	11.8(sh, 23), 13.0(sh, 35), 14.1(81), 15.2(87), 16.0(sh, 68), 25.0(sh, 137), 29.6(1200)
NiBr <sub>2</sub> •L	Solid	8.2, 10.8(sh), 13.0, 13.5, 14.7, 19.6(sh), >25.0
	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	11.3, 13.0, 31.3(5930)
	CH <sub>3</sub> NO <sub>2</sub>	9.1(sh, 40), 13.0(86), 25.0(815).
NiI <sub>2</sub> •L	Solid	9.3, 10.3(sh), 11.1, 12.8(sh), 19.1(sh), >25.0
	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	11.4(sh, 30), 12.9(63), 23.5(3500), 31.7(7510)
	CH <sub>3</sub> NO <sub>2</sub>	8.7(20), 12.4(54), 25.0(3400)
Ni(NCS) <sub>2</sub> •L	Solid	5.18, 5.72, 6.3, 6.7, 8.34(sh), 10.9, 21.8(sh), 29.4
Ni(N <sub>3</sub> ) <sub>2</sub> •L	Solid	10.5, 21.0, >29.4
[NiL <sub>2</sub> ][Ni(CN) <sub>4</sub> ]	Solid	12.1, 18.2(sh), 26.7
	CH <sub>3</sub> NO <sub>2</sub>	12.3(98)
[NiL <sub>2</sub> ]Br <sub>2</sub>	Solid	12.2, 18.2(sh)
	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	12.2, 31.3(sh, 9500)
[NiL <sub>2</sub> ]I <sub>2</sub>	Solid	12.35, 18.2(sh)
	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	12.25(76)
	CH <sub>3</sub> NO <sub>2</sub>	12.2(96), 18.2(sh, 145), 28.8(4540)
[NiL <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Solid	12.2, 18.2(sh)
	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	12.2(89)
[NiL' <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Solid	12.1 >25.0
	CH <sub>3</sub> NO <sub>2</sub>	12.2(93), 26.3(5340)
[NiL'' <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> •H <sub>2</sub> O	Solid	12.2, 18.2(sh)
	CH <sub>3</sub> NO <sub>2</sub>	12.1(78)
[NiL''' <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Solid	12.3
	CH <sub>3</sub> NO <sub>2</sub>	12.3(42)

plexes with the other ligand derivatives (II) all contain five-coordinate nickel(II) atoms. The evidence for five-coordination comes from the stoichiometry, electrical conductance, and far infrared and electronic spectral measurements. The conductivities in nitromethane (Table II) indicate partial solvolytic displacement of coordinated anions and indeed, NiCl<sub>2</sub>•L'''•H<sub>2</sub>O has a value typical of a 1:1 electrolyte [11]. However, for those complexes soluble in dichloroethane, the molar conductivities are less than 3.5% of the values expected for 1:1 electrolytes at the same concentration and thus the complexes are practically undissociated. The monomeric nature of the complexes in dichloroethane could not be

confirmed by molecular weight measurements because the complexes have insufficient solubility for a determination. A value of 300 for NiI<sub>2</sub>•L in nitromethane corresponds to extensive dissociation.

Electronic spectra were measured both in the solid state and in solution in dichloroethane (for those complexes having sufficient solubility) and in nitromethane. Band maxima and molar extinction coefficients are reported in Table III. Solution spectra in dichloroethane and in general also in nitromethane are in good agreement with the Nujol mull transmittance spectra, with respect to both band position and relative intensities of the bands. Thus, the halide complexes dissolve in dichloroethane without

configurational rearrangement, though solvolysis is appreciable in some cases in nitromethane (as evidenced by the conductivities).

The electronic spectra of the halide complexes are very similar to each other and are typical of high-spin five-coordinate nickel(II) complexes. The major band in the region 11.0–14.0 kK is quite broad and is apparently composed of two or three components. The less intense band in the region 8.3–9.3 kK is a very broad shoulder to the major band. Another band observed at 19.2 kK as a shoulder in some instances is obscured by the more intense charge-transfer bands that occur above 25.0 kK. A weak peak near 5.9 kK that is observed for all of the complexes in this paper can be assigned to a vibrational overtone. The spectra fit reasonably well with that expected from the complete energy level diagrams for nickel in either a trigonal bipyramidal or square pyramidal environment with a  $N_3X_2$  donor set [12–14]. Judge and Baker [8] have suggested that the magnetic and spectral properties of nickel and cobalt halide complexes of terpy are best interpreted by a square pyramidal treatment. Subsequent X-ray single crystal analysis [15] showed that the actual geometry in  $CoCl_2 \cdot terpy$  is intermediate between the two limiting five-coordinate configurations; a similar situation was shown earlier for the structure of  $ZnCl_2 \cdot terpy$  [16]. Since we have shown [17] by X-ray analysis of the structure of  $LNi(NO_3)_2$  that 2,6-diacetylpyridinebis(anil) contains a planar terdentate NNN donor set, similar to that of terpy, we can reasonably assign distorted pentacoordinate structures to the present nickel halide complexes of the ligands II. Structural determinations for other five-coordinate complexes have shown that such intermediate geometries are to be expected [18].

Harris and Lockyer [8] also reported several nickel(II) complexes of terpy and formulated the halogeno complexes as dimeric salts  $[Ni(terpy)_2][NiX_4]$ . Comparison of our spectral data for the complexes of the ligands (II) with their diffuse reflectance spectra clearly shows that such a formulation is inappropriate for our complexes. The magnetic moments of the present halide complexes are in the range 3.1–3.3 B.M. as expected for high-spin five coordinate nickel(II) complexes [12], whilst the complexes formulated as  $[Ni(terpy)_2][NiX_4]$  have values in the range 3.36–3.64 B.M. in agreement with the presence of tetrahedral halogeno anions. It is pertinent that the dimeric salts of terpy were obtained [8] by reaction with excess  $[NiX_4]^{2-}$  ions, unlike our experimental conditions.

Additional evidence for pentacoordination in the chloro- and bromo-complexes is available from the infrared spectral bands observed in the 400–150  $cm^{-1}$  region (Table II). Strong M–X stretching bands that are resolved into symmetric and asymmetric stretching modes occur in the 200–300  $cm^{-1}$  region,

with the  $\nu(Ni-Br)/\nu(Ni-Cl)$  ratio being *ca.* 0.81 for the bands in the  $NiX_2 \cdot L$  case. Similarly, a deformation mode near 240  $cm^{-1}$  in all of the chloro complexes occurs at 196  $cm^{-1}$  in the bromide. No band in the spectrum of  $NiI_2 \cdot L$  can as clearly be assigned to  $\nu(Ni-I)$ , though such an absorption might be expected near 200  $cm^{-1}$ . Assignment of the nickel–chlorine and nickel–bromine frequencies to pentacoordinate species follows previously published data for nickel halide complexes [19, 20] and pentacoordinate metal complexes of terpy [21, 22]. It is especially noteworthy that the observed bands are incompatible with the presence of either octahedral or tetrahedral geometries (*e.g.*  $NiCl_2 \cdot 2py$  and  $NiCl_4^{2-}$  have  $\nu(Ni-Cl)$  at 246  $cm^{-1}$  and 285  $cm^{-1}$ , respectively) [19].

#### Nickel Thiocyanate Complex

Formulation of this complex is not clear-cut but the evidence favors a thiocyanato-bridged octahedral polymer. The strong band at 10.9 kK might be expected nearer 13.0 kK in a five-coordinate structure since thiocyanato- is higher in the spectrochemical series than for the halogen-anions. The magnetic moment and the electronic spectrum is in accord with that expected for six-coordinate, tetragonal nickel(II) and definitely rules out the presence of tetrahedral  $Ni(NCS)_4^{2-}$  [12, 23]. The general insolubility of the complex and the non-conductance in nitromethane support a bridging octahedral structure. The presence of both bridging and non-bridging thiocyanate groups might be expected to lead to two C–N stretching frequencies near 2100  $cm^{-1}$  [23]. The observation of a single broad band at 2090  $cm^{-1}$  may result from accidental overlapping of the two frequencies. Ligand absorptions in the C–S stretching and  $\delta(NCS)$  vibration regions negate the possibility of useful band assignments there. However, another preparation of the complex, which analyzed as the trihydrate and gave an infrared band at 3420  $cm^{-1}$  characteristic of lattice water, exhibited C–N stretching frequencies at 2080  $cm^{-1}$  and 2118  $cm^{-1}$  as expected for two kinds of thiocyanate groups. Similar properties to those above were observed for  $Ni(terpy)(NCS)_2$  [8] and the complexes of two aliphatic analogues of ligand(II) [10].

#### Nickel Azide Complex

Harris and Lockyer formulated their azide complex of (I) as the dimeric compound  $[Ni(terpy)_2][Ni(N_3)_4]$  rather than a polymeric octahedral structure like the thiocyanate compound. Thus, the high (for octahedral) magnetic moment of 3.7 B.M. recalculated as 4.1 B.M. for the presumably tetrahedral  $[Ni(N_3)_4]^{2-}$  anion. A similar representation for our azide complex yields a recalculated magnetic moment (using the experimentally observed [7] susceptibility data for  $[NiL_2](ClO_4)_2$  to account for the paramagnetism of the cation) of 3.65 B.M. for the anion

TABLE IV. Comparison of 10Dq for Terdentate NNN Ligands in  $[\text{Ni}(\text{ligand})_2]^{2+}$  Complexes.

Ligand	10Dq ( $10^{-3}$ kK)	Reference
Terpyridine	12.75 <sup>a</sup>	26
Terpyridine	12.2 <sup>b</sup>	8
Bis(2'-quinolyl)-2,6-pyridine	10.65	27
2,6-Diacetylpyridinebis(hydrazones)	12.6–10.6	28
Substituted tri-(2 pyridyl)amines	12.8–10.45	4
Substituted amidines	11.7–9.0	4
Diethylenetriamine	11.5	1
2,6-Diacetylpyridinebis(anil)	12.2	This Work
2,6-Diacetylpyridinebis( <i>p</i> -methoxyanil)	12.2	"
2,6-Diacetylpyridinebis( <i>p</i> -fluoroanil)	12.2	"
2,6-Diacetylpyridinebis(benzylanil)	12.3	"

<sup>a</sup>Aqueous solution. <sup>b</sup>Solid state.

in a dimer  $[\text{NiL}_2][\text{Ni}(\text{N}_3)_4]$ . Since a value nearer 4.0 B.M. would be expected for the tetrahedral anion, our magnetic data is in agreement with the other evidence that suggests a bridging octahedral structure as for the thiocyanate analogue. The three bands at 10.5, 15.4, and 20.8 kK occur at appropriate positions for octahedral geometry and the characteristic 12.2 kK band of  $[\text{NiL}_2]^{2+}$  is not observed. The slightly lower position of  $\nu_1$  for the azide case as compared to the thiocyanate is in agreement with the lower position of the azide group in the spectrochemical series [24]. The broad infrared band assignable to the azide stretching frequency shows maxima at 2022  $\text{cm}^{-1}$  (vs), 2035  $\text{cm}^{-1}$  (vs) and thus is compatible with the presence of both terminal and bridging azide groups. Similarly the presence of several far-infrared bands in the spectra of the azide and thiocyanate derivatives (Table II) not found for the halide complexes also supports the above formulation of both the azide and the thiocyanate.

#### Nickel Cyanide Complex

As reported [8] for the 1:1 terpyridine complex, our evidence strongly indicates a dimeric formulation,  $[\text{NiL}_2][\text{Ni}(\text{CN})_4]$ . The magnetic moment, found to be 2.22 B.M. based on a monomeric complex, recalculates for a diamagnetic, square planar anion, assuming a value of 3.10 B.M. for the  $[\text{NiL}_2]^{2+}$  cation [7]. The presence of the paramagnetic cation is confirmed by the electronic spectrum (Table III), where  $\nu_1$  occurs at 12.1 kK. The  $\text{Ni}(\text{CN})_4^{4-}$  anion is known to give intense absorption bands only above 30 kK [25]. The single sharp strong infrared absorption at 2120  $\text{cm}^{-1}$  rules out any five coordinate structure as two  $\nu(\text{C}\equiv\text{N})$  stretching vibrations would then be predicted. Final proof of the cation-anion formulation is given by the conductance value of 102 mho  $\text{cm}^2 \text{mol}^{-1}$  in nitromethane [11].

#### Nickel Bis(ligand) Complexes

The six other brown complexes of this type contain octahedral nickel(II) cations and bromide, iodide or tetrafluoroborate anions. The molar conductivities of the complexes in dichloroethane are scarcely above those expected for 1:1 electrolytes, so doubtless ion pairing is extensive, but the values for nitromethane solution are reasonable for 2:1 electrolytes [11]. The molecular weight of  $[\text{NiL}_2]_2$  in nitromethane is 322 which is in agreement with the presence of three ions in solution. The magnetic moments, which vary from 3.05 to 3.20 B.M., are of the order found for high-spin octahedral nickel(II) complexes [12]. The absorption spectra, which are unchanged in dichloromethane, nitromethane, and in the solid state, provide the major evidence for six-coordination. The  ${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$  transition of  $\text{O}_h$  symmetry, corresponding to 10Dq, can be assigned to the band that occurs near 12.2 kK. The second transition is found near 18.2 kK as a shoulder to the much more intense charge-transfer band whose maximum is above 25.0 kK [25.7 kK for  $[\text{ZnL}_2](\text{ClO}_4)_2$ ] [7]. Unfortunately, the difficulty in assigning  $\nu_2$  and  $\nu_3$  transitions for these complexes negates our ability to calculate any other ligand field parameters from the spectra. It is worthwhile, however, to compare the value of 10Dq for these ligands with those of other terdentate NNN donor ligands (Table IV). It is seen that the ligand field strengths of the 2,6-diacetylpyridinebis(imines) are the same within experimental error and very similar to analogous ligands containing at least one pyridyl moiety. Other workers have demonstrated that these ligands lead to magnetic crossover situations in  $[\text{M}(\text{ligand})_2]^{2+}$  ( $\text{M}(\text{II}) = \text{Co}, \text{Fe}$ ) complexes and that steric modification of the ligands will affect the observed multiplicity [4, 27, 28]. Although any difference in electronic effects of the *para*-substituents in the 2,6-diacetylpyridinebis(imines) was not observed in the 10Dq values of the

bis(ligand)Ni(II) complexes, further studies are underway to ascertain their influence on the magnetic behaviour of a series of mono- and bis-ligand Co(II) complexes.

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