

# Synthesis and Characterization of Metal Complexes of Terdentate NNN Donor Ligands Derived from 2,6-Diacetylpyridine. Nickel(II), Copper(II), Zinc(II) and Cadmium(II) Complexes of 2,6-Diacetylpyridinebis(anil) with Both Monodentate and Bidentate Nitrate Groups

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Some divalent metal complexes of 2,6-diacetylpyridinebis(anil), a terdentate NNN donor ligand, having a variety of nitrate bonding modes are reported. The complexes of the type  $ML(NO_3)_2$ ,  $MLCl(NO_3)$ ,  $[ML(en)NO_3]NO_3$  and  $[ML_2](NO_3)_2$  ( $M = Ni(II), Cu(II), Zn(II)$  and  $Cd(II)$ ;  $L = C_{21}H_{19}N_3$ ;  $en = ethylenediamine$ ) are characterized by magnetic moment, conductivity, and NMR, infrared, Raman and electronic spectral measurements. The spectral data is correlated with the metal geometry and the type of nitrate coordination, which includes ionic, monodentate, bidentate, as well as both monodentate and bidentate simultaneously.

## Introduction

The coordinating ability of 2,6-diacetylpyridinebis(imines), (Fig. 1) terdentate NNN donor ligands derived by the Schiff base condensation of 2,6-diacetylpyridine with some aromatic amines, is comparable to that of terpyridine (terpy), the most widely studied of this class of ligand [1]. Characterization of metal complexes of these new versatile ligands has been undertaken in our laboratories [2] and as part of the study of nickel(II) complexes, we isolated  $NiL(NO_3)_2$  where L is the parent 2,6-diacetylpyridinebis(anil) ligand ( $R = C_6H_5$ ) in Fig. 1.

The structure of this complex was of particular interest for two reasons. Firstly, infrared data for analogous nickel complexes [3] had suggested the presence of both monodentate and bidentate nitrate groups in the pseudo-octahedral complexes.

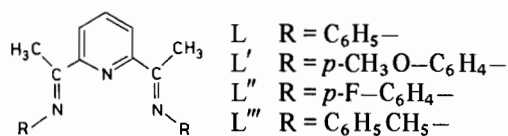


Fig. 1. Structural formula for 2,6-diacetylpyridinebis(imines).

Secondly, the occurrence of both of these nitrate bonding types within one metal complex had only been proved by X-ray analysis for  $VO(NO_3)_3CH_3CN$  [4] and  $(C_5H_5N)_3M(NO_3)_2$  ( $M = Co(II), Cu(II), Zn(II)$ ) [5]. In order to establish the generality of this nitrate bonding situation and to investigate the influence of metal ion size and electronic configuration we have isolated the complexes of the type  $ML(NO_3)_2$ ,  $MLCl(NO_3)$ ,  $[ML(en)NO_3]NO_3$ , and  $[ML_2](NO_3)_2$  ( $M = Ni(II), Cu(II), Zn(II)$  and  $Cd(II)$ ;  $L = C_{21}H_{19}N_3$ ). Characterization of these divalent metal complexes having a variety of nitrate bonding types by magnetic moment, conductivity, and NMR, infrared, Raman and electronic spectral measurements are the subject of this paper. The X-ray structural determinations of the  $NiL(NO_3)_2$  and  $CuL(NO_3)_2$  derivatives have been reported elsewhere [2(e), 2(f), 6].

## Experimental

### Chemicals

The terdentate NNN donor ligand 2,6-diacetylpyridinebis(anil) was prepared as previously described [2(c)]. Hydrated metal salts and sodium tetrafluoroborate were obtained from Alfa Inorganics, Inc. Solvents for preparations and other chemicals were reagent grade and were used as received. Solvents

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used for physical measurements were fractionally distilled by standard methods.

#### Physical Measurements

NMR, electronic spectral, magnetic susceptibility and conductivity measurements were performed as described previously [2(c)]. Infrared spectra in the region 4000–200  $\text{cm}^{-1}$  were recorded on a Beckman IR-12 spectrophotometer as Nujol or Halocarbon mulls between KBr or CsI plates. Spectra were also recorded for KBr discs on a Perkin-Elmer 621 instrument. Raman spectra were primarily obtained for KBr discs or acetonitrile solutions on a Cary 83 instrument with a He-Ne laser source; some spectra were obtained for samples in capillaries with a Jarrell-Ash spectrophotometer using an Ar source.

#### Preparation of Complexes

Only the details for a representative complex of each type is given, as the other Ni, Cu, Zn and Cd nitrate complexes of 2,6-diacetylpyridinebis(anil) were readily obtained in high yields by a similar manner. In all cases 2,2-dimethoxypropane was employed to dehydrate the metal salt prior to addition of the ligand and the isolated product was dried *in vacuo* for several hours at room temperature.

##### $\text{CdL}(\text{NO}_3)_2$

To a warm solution of 0.97 g (3.1 mmol)  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in 20 ml absolute ethanol containing 3 ml 2,2-dimethoxypropane, previously refluxed for 15 min, was added 0.90 g (2.9 mmol) of the Schiff base ligand dissolved in 70 ml hot absolute ethanol. After heating and stirring the yellow solution for 1 hr, the volume was reduced to *ca.* 20 ml., resulting in precipitation of the product. Recrystallization from dichloromethane/ether gave a yellow crystalline product; yield, 70%. The analogous Cu, Ni, and Zn derivatives were prepared in 74–85% yield in an analogous fashion [2(f)].

##### $[\text{CuL}_2](\text{NO}_3)_2$

To a warm solution of 1.32 g (5.5 mmol)  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 25 ml absolute ethanol containing 5 ml 2,2-dimethoxypropane, which had been refluxed for ½ hr, was added 4.59 g (15.1 mmol) of the terdentate NNN donor ligand in 250 ml hot ethanolic solution. The dark green solution was heated for 1 hr, concentrated to *ca.* 15 ml and cooled in a refrigerator overnight. The green powder so obtained was recrystallized from dichloromethane; yield, 72%.

##### $\text{ZnLCl}(\text{NO}_3)$

A 0.80 g (2.6 mmol) sample of the ligand dissolved in dichloromethane was added to a warm solution prepared by mixing dehydrated ethanolic solutions of

0.75 g (2.75 mmol)  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.34 g (2.5 mmol)  $\text{ZnCl}_2$ . Heating the yellow solution for 1 hr and reduction of the volume to 20 ml on a rotary evaporator gave a yellow crystalline product that was recrystallized from dichloromethane/ethanol; yield 74%.

##### $[\text{NiL}(\text{en})](\text{NO}_3)]\text{NO}_3$

A green solution of 0.5 g (1.7 mmol)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in *ca.* 50 ml of warm absolute ethanol turned blue as 0.1 g (1.2 mmol) ethylenediamine in ethanol was slowly added. To this solution was added 0.55 g (1.8 mmol) of the Schiff base ligand and the resultant deep brown solution was heated and stirred for ½ hr. Reduction of the volume by half and cooling gave a red-brown crystalline product; yield, 41%.

## Results and Discussion

In the course of an investigation [2] of the nickel(II) complexes of 2,6-diacetylpyridinebis(imines), we found that  $\text{NiL}(\text{NO}_3)_2$  ( $\text{R} = \text{C}_6\text{H}_5$  in Fig. 1) contained both monodentate and near symmetrically bidentate nitrate groups [2(f)]. X-ray analysis of the series of complexes  $(\text{C}_5\text{H}_5\text{N})_3\text{M}(\text{NO}_3)_2$  ( $\text{M} = \text{Co}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II}), \text{Cd}(\text{II})$ ) [5, 7] had already established that significant differences in the chelating ability of the nitrate group exist for the various divalent metals. In an attempt to determine how the nitrate bonding ability varied in a series of complexes involving a terdentate NNN donor ligand, we also prepared  $\text{ML}(\text{NO}_3)_2$  ( $\text{M} = \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II}), \text{Cd}(\text{II})$ ) for  $\text{L} = 2,6\text{-diacetylpyridinebis}(\text{anil})$ . Subsequently, a single crystal X-ray analysis verified a similar pseudo-octahedral geometry in which the bidentate nitrate group is very asymmetrically bonded to the copper atom [6]. In order to characterize the  $\text{ML}(\text{NO}_3)_2$  complexes by spectral means, related complexes that contained potentially ionic, monodentate and bidentate nitrate groups were also studied. The characterization of these various types of complexes are discussed below. Some physical properties and analytical data for the complexes are given in Table I.

##### Complexes of the type $[\text{ML}_2](\text{NO}_3)_2$

Although the bis ligand complexes were readily isolated for  $\text{M}(\text{II}) = \text{Ni}, \text{Cu},$  and  $\text{Zn}$ , the corresponding cadmium derivative could not be freed of impurities without decomposition. All three isolated complexes have conductivities in nitromethane in agreement with that expected [8] for 2:1 electrolytes (Table I).

TABLE I. Some Physical Properties and Analytical Data of the Complexes of 2,6-Diacetylpyridinebis(anil).

Compound	Color	M.P. (°C)	$\Lambda_m^a$	%Carbon <sup>b</sup>	%Hydrogen <sup>b</sup>	%Nitrogen <sup>b</sup>
[NiL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Red-brown	278–279	173	62.3(62.3)	4.8(4.7)	13.7(13.9)
[CuL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Green	211	159	61.4(61.9)	4.5(4.7)	13.3(13.7)
[ZnL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Yellow	210–215d	153	61.2(61.8)	4.9(4.7)	13.4(13.7)
NiLCl(NO <sub>3</sub> )	Dark brown	283–285d	6.0	53.8(53.7)	4.3(4.1)	11.8(11.9)
NiLBr(NO <sub>3</sub> )	Dark brown	>260d	9.0	49.1(48.9)	3.7(3.9)	10.9(10.8)
ZnLCl(NO <sub>3</sub> )	Pale yellow	154–158d	1.9	53.0(53.0)	4.0(4.0)	11.6(11.8)
CdLCl(NO <sub>3</sub> )	Pale yellow	154–155d	9.0	43.3(43.1)	3.4(3.3)	9.7(9.6)
[NiL(en)(NO <sub>3</sub> )](NO <sub>3</sub> )	Red-brown	220	84	49.7(49.8)	4.9(4.9)	17.6(17.4)
[ZnL(en)(NO <sub>3</sub> )](PF <sub>6</sub> )	Pale yellow	195	126	<sup>c</sup> (42.8)	4.2(4.2)	12.8(13.0)
NiL(NO <sub>3</sub> ) <sub>2</sub>	Red-brown	268–270d	36	50.8(50.8)	3.9(4.0)	14.1(14.0)
CuL(NO <sub>3</sub> ) <sub>2</sub>	Green	207	39	50.5(50.4)	4.2(3.8)	14.0(14.0)
ZnL(NO <sub>3</sub> ) <sub>2</sub>	Yellow	205–215d	5.0	50.4(50.2)	3.8(3.8)	13.9(13.9)
CdL(NO <sub>3</sub> ) <sub>2</sub>	Pale yellow	135–137d	14	45.6(45.9)	3.4(3.5)	12.6(12.8)

<sup>a</sup>Molar conductance values (ohms<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) on freshly prepared *ca.* 10<sup>-3</sup> M solutions in nitromethane. <sup>b</sup>Calculated percentage in parenthesis. <sup>c</sup>Irreproducibly low.

TABLE II. Nitrate Infrared Bands of the Complexes (cm<sup>-1</sup>).<sup>a</sup>

Compound	$\nu_3$	$\nu_1$	$\nu_2$	$\nu_4$
[NiL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1330–1390vs,b	1030m	825s	720m
[CuL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1330–1380vs,b	1025ms	830s	720w
[ZnL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1330–1380vs,b	1025m	820s	725m
NiLCl(NO <sub>3</sub> )	1490vs,b 1280vs	1025m	830m	730mw
NiLBr(NO <sub>3</sub> )	1485vs 1280vs	1018m	810m	722mw
ZnLCl(NO <sub>3</sub> )	1480vs 1290vs	1025ms	820ms	725m
CdLCl(NO <sub>3</sub> )	1485vs 1285vs	1020ms	815s	725m
[NiL(en)(NO <sub>3</sub> )](NO <sub>3</sub> )	1340–1380vs,b 1430vs 1305vs	1020s, 1010s	820s	750m, 720m
[ZnL(en)(NO <sub>3</sub> )](PF <sub>6</sub> )	1440vs 1280vs	1020ms	–	740w
NiL(NO <sub>3</sub> ) <sub>2</sub>	1512sh 1502vs 1272vs 1455vs 1288vs	1030, 1020ms	830m, 820ms, 810m	745m, 730m, 710m
CuL(NO <sub>3</sub> ) <sub>2</sub>	1490vs 1290vs 1450w 1310sh 1420s,b	1030sh, 1020ms	830m, 810ms	740w, 725m, 705m
ZnL(NO <sub>3</sub> ) <sub>2</sub>	1485vs,b 1290vs 1430w 1305vs	1015s, 1020s	825sh, 815s	745m, 725m, 705m
CdL(NO <sub>3</sub> ) <sub>2</sub>	1480vs 1280vs,b 1450m,b	1020ms	815ms	740m, 720m

<sup>a</sup>Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad. <sup>b</sup>L = 2,6-diacetylpyridinebis(anil), C<sub>21</sub>-H<sub>19</sub>N<sub>3</sub>.

The infrared spectra of these complexes all show the characteristic strong broad absorption centered at 1360 cm<sup>-1</sup> due to the  $\nu_3$  asymmetric N–O stretch (doubly degenerate (E')) in D<sub>3h</sub> symmetry) of ionic

nitrate. Other bands [3a, 9] (Table II) at 830 cm<sup>-1</sup> and 720 cm<sup>-1</sup> are the  $\nu_2$  out of plane of deformation (A<sub>2</sub>' in D<sub>3h</sub> symmetry) and the  $\nu_4$  in-plane bend (doubly degenerate (E')) in D<sub>3h</sub> symmetry), respec-

TABLE III. Raman Bands of the Zinc and Cadmium Complexes.<sup>a</sup>

Compound		
L <sup>b</sup>	s <sup>c</sup>	1640vs, 1590ms, 1570ms, 1445w, 1320s, 1220s, 1170w, 990s
[ZnL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	s l <sup>d</sup>	1620vs, 1585vs, 1565vs, 1450mb, 1315s, 1250s, 1220s, 1020s, 95m 1625vs, 1590vs, 1570vs, 1460sh, 1450m, 1320vs, 1255m, 1225ms, 1170w, 1120m, 1025vs, 995ms
ZnLCl(NO <sub>3</sub> )	s l l <sup>e</sup> l <sup>e</sup>	1635s, 1590s, 1570s, 1460mb, 1320m, 1255w, 1225w, 1115w, 1025m, 1000sh 1630vs, 1590s, 1570s, 1440vs,b, 1315s, 1250mw, 1220s, 1020s, 995m 1630vs, 1590s, 1570s, 1440vs,b, 1315s, 1250mw, 1220s, 1020s, 995m 1630m, 1600m, 1590m, 1570m, 1440s,b, 1260m
CdLCl(NO <sub>3</sub> )	s l	1635vs, 1590vs, 1570vs, 1450mb, 1310s, 1250s, 1220vs, 1015vs, 995s 1630vs, 1590s, 1570s, 1440sb, 1310s, 1250ms, 1220vs, 1020vs, 995s
ZnL(NO <sub>3</sub> ) <sub>2</sub>	s	1630vs, 1595s, 1570s, 1460w, 1440w, 1318sh, 1260s, 1225s, 1175wb, 1115mw, 1030s, 1000m
CdL(NO <sub>3</sub> ) <sub>2</sub>	s l <sup>f</sup> l <sup>f</sup>	1625s, 1590s, 1570s, 1440mb, 1310m, 1250s, 1220s, 1170w, 1025s, 1000m 1635vs, 1590s, 1570s, 1520w, 1480sh, 1450sb, 1420sh, 1310ms, 1250ms, 1220s, 1100w, 1030sh, 1015s, 995s 1635s, 1600s, 1575s, 1500w, 1460wb, 1260m, 1180mb, 1100wb, 1040w, 1010w, 995w

<sup>a</sup>Bands are listed for the range 1650–950 cm<sup>-1</sup>. See footnote, Table II, for abbreviations. <sup>b</sup>L = 2,6-diacetylpyridinebis(anil), C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>. <sup>c</sup>Solid spectrum recorded for spinning KBr disc. <sup>d</sup>Liquid spectrum recorded for spinning (saturated) acetonitrile solution. <sup>e</sup>Similar spectrum recorded for CdLCl(NO<sub>3</sub>). <sup>f</sup>Similar spectrum recorded for ZnL(NO<sub>3</sub>)<sub>2</sub>.

TABLE IV. Electronic Spectra for the Nickel and Copper Complexes.

Compound	Nitromethane solution 10 <sup>-3</sup> cm <sup>-1</sup> <sup>a</sup>	Solid-State 10 <sup>-3</sup> cm <sup>-1</sup> <sup>b</sup>
[NiL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	12.5(73), 26.9(1240)	12.0, 19.8, 27.8
[CuL <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	14.2(158), 24.4(271)	13.0, 13.8
NiLCl(NO <sub>3</sub> ) <sup>c</sup>	10.4(41), 10.7(41), 15.4(18), 29.2(1360)	10.3, 10.6, 15.9, 20.9
NiLBr(NO <sub>3</sub> )	—	11.3, 12.1, 19.2
NiL(NO <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	11.2(46), 12.5(34), 15.4(1180), 29.4(69)	11.5, 12.7, 20.0
CuL(NO <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	14.4(120), 25.0(288)	14.3, 19.5, 26.7

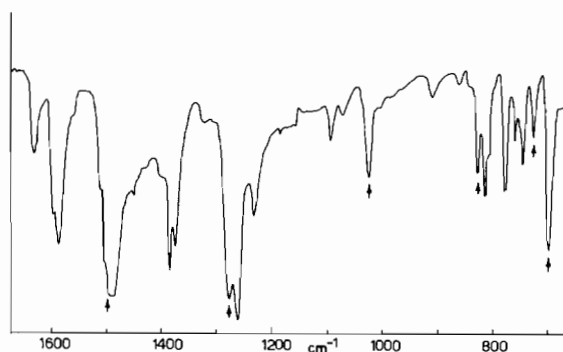
<sup>a</sup>Molar extinction coefficients are given in parenthesis. <sup>b</sup>Transmission spectrum of a Nujol mull of the solid complex suspended on filter paper. <sup>c</sup>Solution spectrum is for an acetonitrile solution.

tively. The  $\nu_2$  and  $\nu_3$  bands are broadened by ligand bands in the same region, but are nevertheless characteristic of ionic nitrate groups. The polarized band at 1025 cm<sup>-1</sup> due to N–O symmetric stretch is a prominent feature of the Raman spectrum of [ZnL<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (Table III). The nickel complex shows electronic transitions (Table IV) that can be assigned to those expected for octahedral symmetry, and 10 Dq = 12,200 cm<sup>-1</sup> as found for other [NiL<sub>2</sub>]Y<sub>2</sub> complexes (Y = Br, I, BF<sub>4</sub>, ClO<sub>4</sub>) [2]. The ligand field strength of 2,6-diacetylpyridinebis(anil) is thus virtually identical to that of terpyridine [10]. The

asymmetrical band in the absorption spectrum of [CuL<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> moves to slightly higher energy for an acetonitrile solution but is in the appropriate region for octahedral geometry [11]. The magnetic moments of the bis(ligand) derivatives of Ni(II) and Cu(II) (Table V) are also as expected for octahedral cations, though such values are not definitive of six-coordination [11, 12]. The methyl resonance in the NMR spectrum of the [ZnL<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> complex occurs as a singlet at 2.47  $\delta$  in DMSO-d<sub>6</sub> which is downfield from that in the free ligand [2(c)], as is characteristic of the ligand showing terdentate behaviour.

TABLE V. Magnetic Data for the Nickel and Copper Complexes.

Compound	$10^6 \chi_g$	$10^6 \chi_M^{\text{corr}}$	$\mu_{\text{eff}}$ , B.M.	Temp. °C
$[\text{NiL}_2](\text{NO}_3)_2$	4.85	4238	3.19	25.0
$\text{NiLCl}(\text{NO}_3)$	8.65	4243	3.19	25.0
$\text{NiLBr}(\text{NO}_3)$	7.98	4293	3.20	23.0
$\text{NiL}(\text{NO}_3)_2$	8.13	4217	3.17	23.0
$[\text{NiL}(\text{en})(\text{NO}_3)]\text{NO}_3$	7.04	4097	3.13	23.0
$[\text{CuL}_2](\text{NO}_3)_2$	1.76	1744	2.05	25.0
$\text{CuLCl}(\text{NO}_3)$	3.45	1819	2.09	24.0
$\text{CuL}(\text{NO}_3)_2$	2.89	1631	1.98	23.5

Fig. 2. Infrared spectrum of  $\text{NiLCl}(\text{NO}_3)$ .

#### Complexes of the type $[\text{MLX}(\text{NO}_3)]$

The complexes of this type were expected to contain bidentate nitrato groups due to the tendency of the metal atoms to achieve six-coordination. The physical evidence for the complexes with  $\text{M} = \text{Ni}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{M} = \text{Zn}$ ,  $\text{Cd}$ ,  $\text{X} = \text{Cl}$  support this expectation. A dark green copper complex which had properties in agreement with a  $\text{CuLCl}(\text{NO}_3)$  formulation failed to give satisfactory carbon analysis. The conductivities of these complexes in nitromethane were negligible, though signifying that solvolysis occurs to a small extent for these non-electrolytes. The NMR spectra of the diamagnetic complexes show a small but significant downfield shift of the methyl resonance that is indicative of terdentate ligand behaviour [2].

The infrared spectra of this group of nitrato complexes, as exemplified by Fig. 2, clearly demonstrate the presence of bidentate nitrato groups. With the binding of two of the oxygen atoms, the nitrato moiety is reduced to  $\text{C}_{2v}$  symmetry, and thus the double degeneracy of the  $\nu_3$  and  $\nu_4$  bands is lifted and splitting into  $\text{A}_1$  and  $\text{B}_1$  modes is expected [9]. The strong broad band due to ionic nitrate at  $1360 \text{ cm}^{-1}$  ( $\nu_3$ ) is now absent, with only a medium to

weak band (found in the ligand and non-nitrato ligand complexes) being observed in this region. The two new bands associated with the asymmetric stretch appear near  $1490 \text{ cm}^{-1}$  ( $\text{A}_1$ ) and  $1280 \text{ cm}^{-1}$  ( $\text{B}_1$ ), respectively, and give clear evidence for bidentate nitrato behaviour. Observation of the splitting of the  $720\text{--}730 \text{ cm}^{-1}$  band ( $\nu_4$ ) was not possible due to the presence of a strong ligand band at  $700 \text{ cm}^{-1}$ .

Addison *et al.* [9] stated that "the relative intensities of the three highest frequency Raman shifts, together with their depolarization ratios, currently provide the most acceptable means of distinguishing between the two extremes of unidentate and symmetrically bidentate co-ordination of the nitrate group to metals". Unfortunately, all of the nickel and copper complexes reported in this paper were decomposed by either an Ar or a He-Ne laser source, though some weak spectra were obtained using spinning KBr discs for sample support. The Raman data reported in Table III for the zinc and cadmium complexes were obtained for spinning KBr discs or acetonitrile solutions using the He-Ne laser source.

With bidentate nitrato groups the  $\text{A}_1$  bands should be strong and polarized and the  $\text{B}_1$  band, weak and depolarized. As listed in Table III and illustrated for  $\text{ZnLCl}(\text{NO}_3)$  in Fig. 3, the bands near  $1450 \text{ cm}^{-1}$  and  $1030 \text{ cm}^{-1}$  are polarized whilst the band near  $1260 \text{ cm}^{-1}$  is depolarized. The relative Raman intensities for these three N-O stretching bands are also in the sequence found for bidentate nitrato groups [9] and thus we conclude that the complexes of the type  $\text{MLCl}(\text{NO}_3)$  ( $\text{M} = \text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$ ) are six-coordinate.

Further evidence that the complexes  $\text{NiLX}(\text{NO}_3)$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) are also octahedral via nitrato chelation is obtained from their electronic spectra (Table IV, Fig. 4). The spectra resemble closely those of  $\text{NiL}(\text{NO}_3)_2$  (*vide infra*) rather than those observed [2] for  $\text{NiLX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ), which are pentacoordinate complexes. Since  $\text{Cl} > \text{Br}$  in ligand field strength,

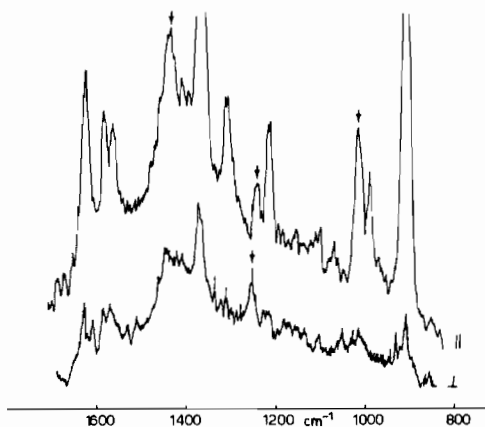


Fig. 3. Solution Raman spectrum of  $\text{ZnLCl}(\text{NO}_3)$ .

we can assign the bands at  $15,900\text{ cm}^{-1}$  and  $10,600\text{ cm}^{-1}$ ,  $10,300\text{ cm}^{-1}$  in the solid state spectrum of  $\text{NiLCl}(\text{NO}_3)$  to the components of the  $\nu_1$  transition in octahedral symmetry, which is expected to be split in the asymmetrical ligand field [12]. The similarity of the solid and solution electronic absorption spectra indicate that the same geometry is found in both states. For the bromide complex, the two lower components of the split  $\nu_1$  band occur at  $11,250\text{ cm}^{-1}$  and  $12,100\text{ cm}^{-1}$  and  $\nu_2$  is assigned as the  $19,200\text{ cm}^{-1}$  band (*i.e.*, at slightly lower energy than for Cl).

#### Complexes of the type $[\text{ML}(\text{en})(\text{NO}_3)]\text{NO}_3$

This type of complex was prepared with the expectation that the coordinated nitrate group would be monodentate and the resultant vibrational spectra would be helpful in characterizing the mode of nitrate bonding in the  $\text{ML}(\text{NO}_3)_2$  complexes. Unfortunately, isolation of these complexes proved very difficult and satisfactory elemental analysis was only achieved for  $[\text{NiL}(\text{en})(\text{NO}_3)](\text{NO}_3)$  and  $[\text{ZnL}(\text{en})(\text{NO}_3)](\text{PF}_6)$ . The latter precipitated following the addition of 2,6-diacetylpyridinebis(anil), ethylenediamine, and ammonium hexafluorophosphate successively as ethanolic solutions to a warm ethanolic  $\text{Zn}(\text{NO}_3)_2$  solution. The conductivities of these two compounds in nitromethane are indicative of 1:1 electrolytes and the NMR spectrum of the zinc complex gives peaks as expected for coordinated terdentate ligand and ethylenediamine.

The infrared nitrate bands for this type of complex are assigned in Table II. The broad band at  $\sim 1360\text{ cm}^{-1}$  ( $\nu_3$ ) as well as the  $720\text{ cm}^{-1}$  ( $\nu_4$ ) and  $830\text{ cm}^{-1}$  ( $\nu_2$ ) bands give evidence for ionic nitrate. Additional peaks due to the monodentate nitrate group appear at  $1305\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$ ; the difference of  $125\text{ cm}^{-1}$  corresponds well with the reported values [3a, 8, 10]. The weak shoulder at  $750\text{ cm}^{-1}$  may be the second component of the split



Fig. 4. Solid-state electronic spectra of the nickel complexes: A,  $\text{NiL}(\text{NO}_3)_2$ ; B,  $\text{NiLBr}(\text{NO}_3)$ ; C,  $[\text{NiL}_2]\text{Y}_2$ .

$\nu_4$  band is monodentate nitrate binding while the other expected band is probably obscured by the strong terdentate ligand band at  $695\text{ cm}^{-1}$ . Infrared peaks at  $3360\text{ cm}^{-1}$  and  $3290\text{ cm}^{-1}$  in the spectrum of  $[\text{ZnL}(\text{en})(\text{NO}_3)]\text{PF}_6$  can be assigned to  $\nu(\text{N-H})$  of coordinated ethylenediamine. Satisfactory Raman data for this compound was not obtained.

#### Complexes of the type $\text{ML}(\text{NO}_3)_2$

The presence of both monodentate and bidentate nitrate groups within the same complex has only been established by X-ray single crystal analysis in two instances [4, 5] although several workers had suggested the occurrence of both nitrate bonding types in certain pseudo-octahedral nickel(II) complexes [3]. Our observation of analogous infrared spectral data for  $\text{NiL}(\text{NO}_3)_2$  prompted the current investigation. Preliminary structural characterization of  $\text{NiL}(\text{NO}_3)_2$  and X-ray analysis of  $\text{ML}(\text{NO}_3)_2$  ( $\text{M} = \text{Ni}(\text{II}), \text{Cu}(\text{II})$ ) were reported elsewhere [2(d), 2(e), 2(f), 6]. Full spectral assignments and other structural information for the four complexes  $\text{ML}(\text{NO}_3)_2$  ( $\text{M}(\text{II}) = \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$ ) are discussed now.

Although solvolysis of  $\text{NiL}(\text{NO}_3)_2$  is appreciable in nitromethane, the conductance values (Table I) of the complexes of this type rule out any ionic formulation. The absence of the  $\nu_3$  band near  $1360\text{ cm}^{-1}$  in the solid state infrared spectra confirms that only coordinated nitrate groups are present. The typical pattern in the  $\nu(\text{C}::\text{N})$  region of the infrared spectra

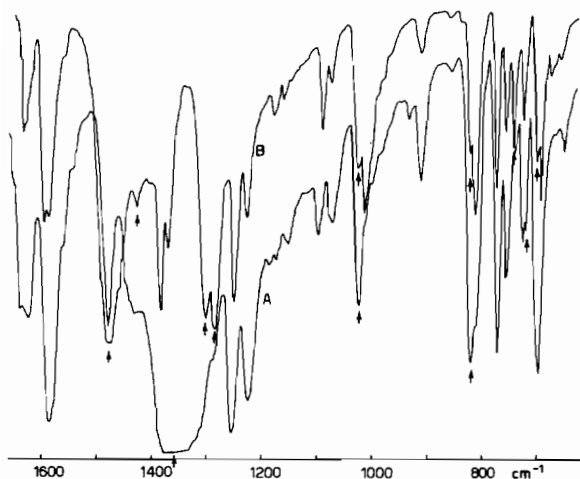


Fig. 5. Infrared spectrum of  $[\text{ZnL}_2](\text{NO}_3)_2$  (A) and  $\text{ZnL}(\text{NO}_3)_2$  (B).

(two bands at *ca.* 1640 and 1590  $\text{cm}^{-1}$ ), as observed for all the metal complexes of the related 2,6-diacetylpyridinebis(imines) studied to date [2] indicate the terdentate behavior of the NNN donor ligand. Similarly, the methyl resonance in the  $\text{ML}(\text{NO}_3)_2$  ( $\text{M}(\text{II}) = \text{Zn}, \text{Cd}$ ) derivatives occurs as a singlet slightly downfield [ $\delta$  2.54 for  $\text{CdL}(\text{NO}_3)_2$  in dichloromethane] from the free ligand position, in agreement with coordination of both azomethine nitrogen atoms.

The solid state electronic absorption bands (Table IV, Fig. 4) for  $\text{NiL}(\text{NO}_3)_2$  indicates pseudo-octahedral geometry as a broad band with maxima at 11,500  $\text{cm}^{-1}$  and 12,700  $\text{cm}^{-1}$  can be assigned to a split  $\nu_1(^3\text{T}_{2g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F}))$  transition. The band at 20,000  $\text{cm}^{-1}$  is due to the  $\nu_2(^3\text{T}_{1g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F}))$  transition so that  $\nu_2/\nu_1$  is approximately 1.65. In acetonitrile solution the components of the  $\nu_1$  transition of octahedral symmetry are still observed but in addition an intense peak occurs at 15,400  $\text{cm}^{-1}$ . The presence of a four-coordinate  $[\text{NiL}(\text{NO}_3)](\text{NO}_3)$  complex would be compatible with the significant conductance values which are found for nitromethane and acetonitrile solutions. Attempts to isolate such four-coordinate  $[\text{MLX}]^+$  cations are the subject of another investigation.

Comparison of the infrared spectra for the  $\text{ML}(\text{NO}_3)_2$  complexes with those observed for the other nitrate complexes reported herein as well as other  $\text{MLX}_2$  and  $[\text{ML}_2](\text{BF}_4)_2$  complexes [2] allows the assignment of both monodentate and bidentate nitrate bonding types (Table II). A typical spectrum, that of the solid state (KBr disc) of  $\text{ZnL}(\text{NO}_3)_2$  is shown in Fig. 5. The doubly degenerate vibrations of ionic nitrate ( $\nu_3$  at 1360  $\text{cm}^{-1}$  in  $\text{D}_{3h}$  symmetry), are replaced by those due to the monodentate nitrate vibrations (at about 1300 and 1450  $\text{cm}^{-1}$ ) and the

bidentate nitrate group (at about 1280 and 1490  $\text{cm}^{-1}$ ). Several terdentate ligand bands occur in the 700–830  $\text{cm}^{-1}$  region and thus our assignments of  $\nu_2$  and  $\nu_4$  bands to the different nitrate moieties can only be tentative; it is significant however, that additional bands occur in this region of the spectra of the  $\text{ML}(\text{NO}_3)_2$  complexes that are not observed for the other types of nitrate complexes individually. Also noteworthy is the observation that the peak attributable to N–O symmetrical stretch ( $\text{A}_1$ ) near 1030  $\text{cm}^{-1}$  is more intense and is split into a doublet as compared to the infrared spectra of  $[\text{ML}_2](\text{NO}_3)_2$  and  $\text{MLX}(\text{NO}_3)$ . This is compatible with the presence of two distinct bonding types for the nitrate groups. This band, which is polarized in the Raman spectra of all the complexes, is also resolved into two components in the Raman spectrum of  $\text{ML}(\text{NO}_3)_2 \cdot (\text{M}(\text{II}) = \text{Zn}, \text{Cd})$ . Solution Raman data for the latter complexes were very similar to those observed for the  $\text{MLCl}(\text{NO}_3)$  complexes (*i.e.* polarization measurements identified the bidentate nitrate bands) and only the additional peak near 1040  $\text{cm}^{-1}$  indicated the presence of a monodentate nitrate group.

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