Synthesis, Magnetic Properties, and Electronic Spectra of Complexes of Nickel(II) Carboxylates with Pyridine and Related Ligands

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Several adducts of nickel(II) carboxylates with the general formula $[NiL_2(O_2CR)_2]$ have been prepared [R = Me, Ph, $4\text{-}ClC_6H_4$, and $2\text{-}NO_2C_6H_4$; L = pyridine (py), 2-methylpyridine (2-Mepy), and quinoline (quin)]. All the complexes have been shown to be six-co-ordinate by magnetochemical and electronic-spectral measurements. Analysis of the tetragonal splitting of their diffuse-reflectance spectra at low temperature and of the polarized single-crystal spectrum of $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$ indicates that all the complexes adopt the *trans*-configuration except $[Ni(2\text{-}Mepy)_2(O_2CPh)_2]$ which shows the *cis*-configuration. No clear evidence has been found for formation of dimeric complexes.

ELECTRONIC spectra of octahedral nickel(II) complexes exhibit three spin-allowed transitions[1] from the $^3A_{2g}$ ground state to the $^3T_{2g}$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ excited states in the regions 7 000—13 000, 11 000—20 000, and 19 000—27 000 cm^{-1} respectively. Two spin-forbidden transitions are often also observed, to ^1E_g (11 000—14 000 cm^{-1}) and $^1T_{2g}$ (18 000—21 000 cm^{-1}). However, these spectra may show tetragonal splittings when two *trans*-directed ligands have markedly different crystal-field strength from the four other ligands. In going from O_h to D_{4h} symmetry many of the excited states are split[2] (Figure 1). Usually splitting of only the $^3T_{2g}$ state is large enough to be measured, but splittings in the higher states have been found in $[NiL_2X_2]$ [L = NH_3, H_2O, pyridine (py), or aniline; X = Cl or Br][3] and in $[NiL_4X_2]$ (L = a substituted aniline; X = ClO_4, Br, or I].[4]

In order to make a systematic assessment of the effects of tetragonal distortions we have prepared a series of complexes of the type $[NiL_2(O_2CR)_2]$ [R = Me, Ph, $4\text{-}ClC_6H_4$, and $2\text{-}NO_2C_6H_4$; L = py, 2-Mepy, or quinoline (quin)] to see if the acid strengths of the parent carboxylic acids are reflected in the Dq values of the anions. The use of a number of heterocyclic amines allowed inductive and steric effects to exert any influence on the structures of the complexes and the Dq values of the donors. The importance of steric effects was shown[5] in methyl- and dimethyl-pyridine complexes with nickel(II) halides, where ligands having methyl groups in the 2-position gave complexes with fewer molecules of base co-ordinated to nickel and tetrahedral, not octahedral, complexes were formed.[6,7] The greatest steric effect occurs in 2,6-dimethylpyridine for which no complexes could be isolated with nickel(II) or cobalt(II) halides, nor were any successfully prepared in this study. This study is somewhat related to investigations of variations in substituents in complexes of metal carboxylates with some stilbenediamines using electronic and n.m.r. spectra,[8] and to a recent report[9] of trifluoroacetato-complexes with pyridine-type ligands, but this latter study did not separate the Dq contributions of the different ligands.

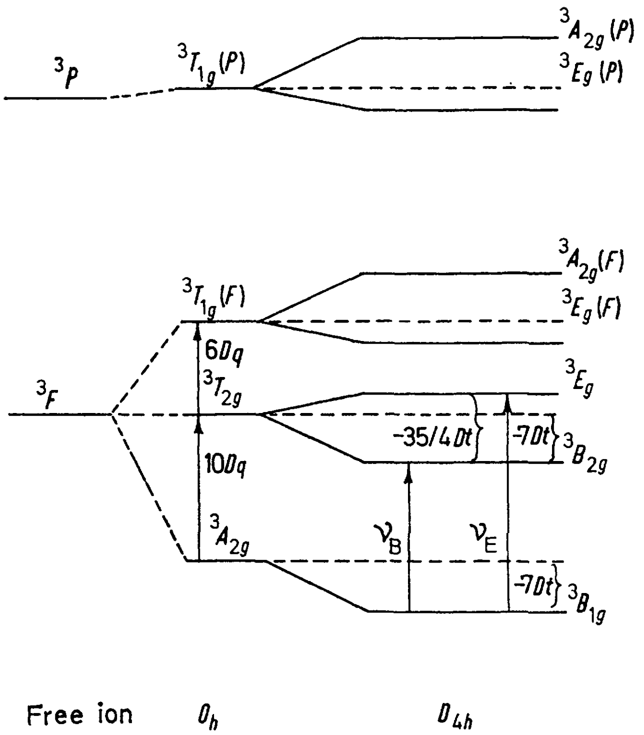

FIGURE 1 Energy levels of d^8 configuration in O_h and D_{4h} symmetries

The complex $[Ni(py)_2(O_2CMe)_2]$ has been prepared previously[10] and was one of the group $[M(py)_n(O_2CR)_2]$ (R = Me, Et, Bu, $CHCl_2$, or CCl_3; M = Ni or Co) designed to investigate the influence of the substituents of the carboxylate group on its behaviour as a uni- or bi-dentate ligand towards bivalent cobalt and nickel.[11] Four molecules of py were co-ordinated with the dichloro- and trichloro-acetates, but two with the other carboxylates. We have already reported[12] the *X*-ray

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[10] T. L. Davis and A. V. Logan, *J. Amer. Chem. Soc.*, 1940, **62**, 1276.

[11] F. Maggio, R. Boacao, R. Cefalù, and V. Romano, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 59.

[12] J. Drew, M. B. Hursthouse, and P. Thornton, *J.C.S. Dalton*, 1972, 1658.

determination of the molecular structure of $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$, originally prepared by Davis and Logan.[10] The molecule is a centrosymmetric monomer with unidentate carboxylate groups, with individual molecules being connected by hydrogen bonds. The electronic spectrum of this complex was also studied as a companion to the others.

An additional incentive to study complexes with pyridine-type bases was the possible formation of binuclear complexes $[Ni_2L_2(O_2CR)_4]$, since for copper(II) 2-chlorobenzoate,[13] α-naphthoate,[14] and formate [15] the py adducts have subnormal magnetic moments where the uncomplexed carboxylate or its hydrates are magnetically dilute, and we have found [16] that $[Co_2(quin)_2(O_2CPh)_4]$ has a binuclear molecular structure.

EXPERIMENTAL

Analyses.—Nickel was determined gravimetrically as its dimethylglyoximate, chlorine by Volhard's method, and carbon, hydrogen, and nitrogen by standard microanalysis in this department or in the Alfred Bernhardt laboratories, with extra oxidant added to ensure complete combustion.

Instrumentation.—Electronic spectra were obtained on a Beckman DK-2A spectrophotometer using 1 cm silica cells for solutions in chloroform, and the standard diffuse-reflectance attachment for solid samples. For studies of reflectance spectra at low temperatures the sample was held between a silica plate and a flat-walled, asbestos-jacketed, white painted, copper vessel filled with liquid nitrogen. A white plate of copper was then used as reference. To prevent ice forming on the sample the attachment was flushed with dry nitrogen before and during use, but this procedure was not always effective. The polarized single-crystal spectra of $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$ were kindly run by Mr. P. Hodgson and Professor B. J. Hathaway at University College, Cork. I.r. spectra were obtained from Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 337 spectrophotometer. Magnetic-susceptibility measurements were made by the Gouy method using a Newport variable-temperature balance over the range 98—323 K at three different field strengths, with calibration by $Hg[Co(NCS)_4]$.[17]

Preparations.—*Diacetatodiaquadipyridinenickel*(II). The procedure was adapted from that of Davis and Logan.[10] Powdered nickel(II) acetate tetrahydrate (3·0 g) was added to excess of pyridine (py) (25 cm^3) to give a green solution, which was filtered while still hot. Light petroleum (b.p. 40—60 °C) was added dropwise to the warm solution until precipitation occurred. After 24 h the pale blue crystals which had been deposited were filtered off, recrystallized from chloroform, washed with diethyl ether, and dried over calcium chloride and concentrated sulphuric acid in a vacuum desiccator (all the amine carboxylate complexes were dried by this procedure, which will not be described each time), yield 4·0 g (93%) (Found: C, 45·35; H, 5·40; N, 7·55; Ni, 15·95. Calc. for $C_{14}H_{20}N_2NiO_6$: C, 45·3; H, 5·40; N, 7·55; Ni, 15·85%), μ = 3·11 B.M.*

Diacetatodipyridinenickel(II). Our attempts to prepare this complex by the earlier method [10,11] always gave the bis(aqua) complex described above. Nickel(II) acetate tetrahydrate (3·0 g) was heated and stirred with acetic anhydride (40 cm^3) for 2 h to give a bright green solution. Rotary evaporation to dryness yielded the yellow-green anhydrous nickel(II) acetate. Pyridine (20 cm^3) was added, and the resulting bright blue solution was stirred at room temperature for 15 min. The pale blue complex was precipitated, filtered off, recrystallized from ethanol, washed with diethyl ether, and dried as before, yield 3·1 g (81%) (Found: C, 49·9; H, 4·85; N, 8·35; Ni, 17·6. Calc. for $C_{14}H_{16}N_2NiO_4$: C, 50·2; H, 4·80; N, 8·35; Ni, 17·55%), μ = 3·19 B.M.

Diacetatobis(2-*methylpyridine*)*nickel*(II). Anhydrous nickel(II) acetate was prepared as described above. 2-Methylpyridine (2-Mepy) (25 cm^3) was added, and the resulting solution was heated under reflux for 2 h. This yielded a green-blue solution, which was filtered hot. On cooling, the pale green-blue complex was precipitated, filtered off, washed with diethyl ether, and dried as before, yield 2·8 g (64%) (Found: C, 52·7; H, 5·65; N, 7·55; Ni, 16·2. Calc. for $C_{16}H_{20}N_2NiO_4$: C, 52·95; H, 5·50; N, 7·70; Ni, 16·2%), μ = 3·25 B.M.

Diacetatodiquinolinenickel(II). Nickel(II) acetate tetrahydrate (3·0 g) was dissolved in a mixture of ethanol (100 cm^3) and acetic acid (5 cm^3). The acetic acid was added to prevent formation of the pale green ethoxy-compound. Quinoline (30 cm^3) was added to the green solution, which was then heated under reflux for 15 h. Excess of ethanol was removed under reduced pressure, and on standing the solution precipitated the dark green crystalline complex, which was filtered off, washed with diethyl ether, and dried as before, yield 4·3 g (82%) (Found: C, 61·05; H, 4·75; N, 6·60; Ni, 13·7. Calc. for $C_{22}H_{20}N_2NiO_4$: C, 60·75; H, 4·60; N, 6·45; Ni, 13·5%), μ = 3·26 B.M.

Triaquadibenzoatonickel(II). A hot aqueous solution of sodium benzoate (1·4 g) and benzoic acid (0·5 g) was filtered slowly into a hot stirred aqueous solution of nickel(II) sulphate hexahydrate (3·0 g). The benzoic acid prevented formation of nickel(II) hydroxide. A pale green solid was precipitated immediately. This was filtered off and recrystallized from a 0·1% aqueous solution of benzoic acid, repeatedly washed with small portions of hot water, and dried in an oven at 65—70 °C (Found: C, 47·05; H, 4·55; Ni, 16·05. Calc. for $C_{14}H_{16}NiO_7$: C, 47·35; H, 4·50; Ni, 16·55%).

Dibenzoatodipyridinenickel(II). Triaquadibenzoatonickel-(II) (2·0 g) was added slowly to hot py (25 cm^3) and the resulting dark green solution was heated under reflux for 2 h. On standing for 24 h the pale blue complex was precipitated, filtered off, recrystallized from ethanol, washed with diethyl ether, and dried as before, yield 2·2 g (85%) (Found: C, 62·7; H, 4·80; N, 5·85; Ni, 12·9. Calc. for $C_{24}H_{20}N_2NiO_4$: C, 62·5; H, 4·75; N, 6·05; Ni, 12·75%), μ = 3·33 B.M.

Dibenzoatobis(2-*methylpyridine*)*nickel*(II). Triaquadibenzoatonickel(II) (1·0 g) was heated under reflux with 2-Mepy (10 cm^3) for 1 h. The resulting dark green solution was filtered hot, and on cooling the bright green crystalline complex was deposited. This was filtered off, washed with diethyl ether and light petroleum (b.p. 40—60 °C), and dried as before, yield 1·1 g (80%) (Found: C, 63·95; H,

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* 1 B.M. $\simeq 9{\cdot}27 \times 10^{-24}$ A m^2.

[13] J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thompson, *J. Chem. Soc.*, 1965, 6464.

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[16] J. Drew, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J.C.S. Chem. Comm.*, 1973, 52.

[17] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

5·00; N, 5·65; Ni, 11·9. Calc. for $C_{26}H_{24}N_2NiO_4$: C, 64·1; H, 4·95; N, 5·75; Ni, 12·05%), μ = 3·28 B.M.

Dibenzoatodiquinolinenickel(II). Triaquabisbenzoatonickel(II) (2·0 g) was added slowly to hot quinoline (20 cm^3) and heated under reflux for 2 h. The dark green solution was filtered hot and on standing for 24 h deposited the dark green crystalline complex, which was filtered off, washed with diethyl ether, and dried as before, yield 2·5 g (80%) (Found: C, 68·55; H, 4·25; N, 5·20; Ni, 10·45. Calc. for $C_{32}H_{24}N_2NiO_4$: C, 68·75; H, 4·30; N, 5·00; Ni, 10·5%), μ = 3·22 B.M.

Bis(*4-chlorobenzoato*)*nickel*(II). A solution of sodium 4-chlorobenzoate was prepared by dropping sodium hydroxide pellets into a suspension of 4-chlorobenzoic acid (3·0 g) in a mixture of water (50 cm^3) and ethanol (10 cm^3). The solution was made just acid to litmus by adding excess of 4-chlorobenzoic acid, before being filtered slowly into a hot, stirred, concentrated aqueous solution of nickel(II) sulphate hexahydrate. When precipitation was complete, the pale green hydrated salt was filtered off and washed well with hot water. It was then dried *in vacuo* at 65 °C over phosphorus pentaoxide for several days, giving the pale yellow anhydrous compound (Found: C, 45·3; H, 2·70; Cl, 19·15; Ni, 15·85. Calc. for $C_{14}H_{10}Cl_2NiO_4$: C, 45·2; H, 2·70; Cl, 19·1; Ni, 15·8%).

Bis(*4-chlorobenzoato*)*dipyridinenickel*(II). Nickel(II) 4-chlorobenzoate (1·0 g) was dissolved in hot py (10 cm^3) to give a turquoise solution. The excess of py was removed under reduced pressure and light petroleum (b.p. 40—60 °C; 25 cm^3) was added to the resulting viscous liquid. After stirring for 1 h the pale blue complex was filtered off, recrystallized from ethanol, washed with diethyl ether, and dried as before, yield 1·3 g (91%) (Found: C, 54·3; H, 3·55; Cl, 13·35; N, 5·40; Ni, 11·65. Calc. for $C_{24}H_{18}Cl_2N_2NiO_4$: C, 54·6; H, 3·40; Cl, 13·45; N, 5·30; Ni, 11·1%), μ = 3·31 B.M.

Bis(*4-chlorobenzoato*)*bis*(*2-methylpyridine*)*nickel*(II). Nickel(II) 4-chlorobenzoate (1·0 g) was dissolved in hot 2-Mepy (15 cm^3) and the dark green solution was heated under reflux for 1 h. The excess of 2-Mepy was removed under reduced pressure and cooling yielded the bright green complex, which was washed with diethyl ether and dried as before, yield 1·3 g (87%) (Found: C, 55·95; H, 4·10; Cl, 12·8; N, 5·15; Ni, 10·35. Calc. for $C_{26}H_{22}Cl_2N_2NiO_4$: C, 56·15; H, 3·95; Cl, 12·8; N, 5·05; Ni, 10·55%), μ = 3·25 B.M.

Bis(*4-chlorobenzoato*)*diquinolinenickel*(II). Nickel(II) 4-chlorobenzoate (2·0 g) was added slowly to hot quinoline (quin) (25 cm^3). The dark green solution was heated under reflux for 1 h, filtered hot, and the excess of quin was removed under reduced pressure. The pale green complex was deposited on cooling, washed with diethyl ether, and dried as before, yield 2·8 g (80%) (Found: C, 60·95; H, 3·40; Cl, 11·55; N, 4·65; Ni, 9·35. Calc. for $C_{32}H_{22}Cl_2N_2NiO_4$: C, 61·15; H, 3·50; Cl, 11·3; N, 4·45; Ni, 9·35%), μ = 3·25 B.M.

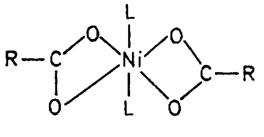
Bis(*2-nitrobenzoato*)*nickel*(II). 2-Nitrobenzoic acid (8·5 g) was suspended in a 1 : 1 mixture of ethanol and water (75 cm^3). Sodium hydroxide pellets were added slowly until the pale brown solution was just basic to litmus. The solution was then made just acid and filtered slowly into a stirred concentrated solution of nickel(II) sulphate hexahydrate (10·0 g) in water. The resulting green solution was concentrated under reduced pressure until precipitation occurred. On standing the pale green crystalline complex was precipitated, filtered off, recrystallized from slightly acidified water, washed with a little hot water, and dried *in vacuo* at 80 °C over phosphorus pentaoxide (Found: C, 54·8; H, 1·60; N, 5·80; Ni, 11·75. Calc. for $C_{14}H_8N_2NiO_2$: C, 54·6; H, 1·65; N, 5·70; Ni, 11·95%).

Bis(*2-methylpyridine*)*bis*(*2-nitrobenzoato*)*nickel*(II). This preparation used the same procedure as that of the corresponding chlorobenzoate complex except that double molar quantities were used, yield 2·0 g (85%) (Found: C, 53·9; H, 3·85; N, 9·70; Ni, 10·25. Calc. for $C_{26}H_{22}N_4NiO_8$: C, 54·1; H, 3·80; N, 9·70; Ni, 10·2%), μ = 3·27 B.M.

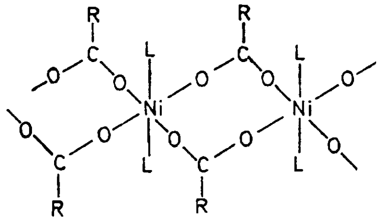
Bis(*2-nitrobenzoato*)*diquinolinenickel*(II). This preparation used the same procedure and molar quantities as the corresponding chlorobenzoate, yield 2·0 g (76%) (Found: C, 59·1; H, 3·40; N, 8·60; Ni, 9·65. Calc. for $C_{32}H_{22}N_4NiO_8$: C, 59·15; H, 3·40; N, 8·65; Ni, 9·05%), μ = 3·26 B.M.

RESULTS AND DISCUSSION

All the complexes prepared in this study contained two molecules of base co-ordinated to each nickel atom. The i.r. spectra, although very sharp, are not a dependable guide to the mode of carboxylate co-ordination, particularly when the bases also have absorptions in the $\nu(CO_2)$ region. However, the absence of unco-ordinated py was shown by the absence of the bands at 601 and 403 cm^{-1} which are shifted on co-ordination.[18] Six-co-ordination was confirmed by the magnetic moments at 298 K (see Experimental section) all having values in the range 3·19—3·33 B.M. These are uncorrected for second-order paramagnetism, but this does not change the value by more than 0·1 B.M. As a check the temperature dependence of the magnetic moment of $[Ni(quin)_2(O_2CMe)_2]$ was investigated and found to be constant within 0·5 B.M. from 323 to 98 K with a negligible θ value of 1·6 K. Six-co-ordination can be achieved by either a monomeric (I) or a polymeric (II) structure. The sketches illustrate *trans*-disposition of the bases and this is deduced to be the case for most of the complexes.



(I)



(II)

The four complexes containing quin are completely insoluble in all solvents, which possibly indicates polymerization, but the py complexes are soluble in several solvents; $[Ni(2\text{-}Mepy)_2(O_2CPh)_2]$ is soluble in chloroform, but the other 2-Mepy complexes only dissolve in chloroform when 10% of the volume of 2-Mepy is added. Attempted molecular-weight determinations in chloroform of the py complexes failed because of partial dissociation, probably by loss of py.

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[18] N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

Electronic Spectra.—The electronic spectra of the complexes were measured at room temperature on solid samples by the diffuse-reflectance technique and where practicable in solution in chloroform or by reflectance at low temperature. The results are collected in Table 1.

(a) *Room-temperature diffuse-reflectance spectra.*—These spectra were all similar and typical of octahedral nickel(II). The ligand-field strengths of the carboxylates and the heterocyclic bases are thus not substantially different, as expected, and *Dt* (Figure 1) was therefore expected to have a small magnitude. The three spin-allowed transitions were observed for all the complexes, but a shoulder at *ca.* 14 000 cm^{-1} was also seen for many of the complexes, and this was assigned as the $^3A_{2g} \rightarrow {}^1E_g$ transition which is most commonly seen when Dq/B approaches unity.[1] ν_1 and ν_3 Were used with Lever's transition-energy-ratio diagrams [1] to calculate values of B and average Dq and to predict values of ν_2 (Table 1). All the calculated values for ν_2 are at lower energies than those observed, probably because ν_2 interacts with the transition to ^1E_g which results in a rather higher ν_2 than theoretically expected.

TABLE 1

Electronic spectra at room temperature

Complex	Medium *	Transition (from $^3A_{2g}$) † ν_1 $^3T_{2g}$	 ^1E_g	 ν_2 (obs.) $^3T_{1g}(F)$	 ν_2 (calc.) $^3T_{1g}(F)$	ν_3 $^3T_{1g}(P)$
$[Ni(py)_2(H_2O)_2(O_2CMe)_2]$	D.r.	9·66	14·5 (sh)	16·26	15·75	27·0
	S.	9·05 (5·8)	13·60	15·62 (7·1)		26·0 (15)
$[Ni(py)_2(O_2CMe)_2]$	D.r.	9·66		16·26	15·75	26·7
	S.	9·09 (6·4)	13·89	15·75 (8·0)		26·0 (16)
$[Ni(2\text{-}Mepy)_2(O_2CMe)_2]$	D.r.	8·81	14·3 (sh)	17·24	14·54	25·3
$[Ni(quin)_2(O_2CMe)_2]$	D.r.	8·97	13·8 (sh)	17·39	14·44	23·8 (sh)
$[Ni(py)_2(O_2CPh)_2]$	D.r.	9·57		16·13	15·60	26·7
	S.	9·22 (7·2)	13·64	16·00 (11)		26·3 (22)
$[Ni(2\text{-}Mepy)_2(O_2CPh)_2]$	D.r.	8·85		15·38	14·60	25·3
	S.	8·77 (6·8)	13·16	15·62 (15)		25·4 (30)
$[Ni(quin)_2(O_2CPh)_2]$	D.r.	9·70	14·18	17·39	15·33	24·1 (sh)
$[Ni(py)_2(O_2C\cdot C_6H_4Cl\text{-}4)_2]$	D.r.	9·01		16·53	14·69	25·3 (sh)
	S.	9·24 (7·3)	13·75	16·00 (11)		26·0 (27)
$[Ni(2\text{-}Mepy)_2(O_2C\cdot C_6H_4Cl\text{-}4)_2]$	D.r.	8·81	13·5 (sh)	15·27	14·54	25·3
$[Ni(quin)_2(O_2C\cdot C_6H_4Cl\text{-}4)_2]$	D.r.	8·85	13·9 (sh)	15·26	14·60	25·6
$[Ni(2\text{-}Mepy)_2(O_2C\cdot C_6H_4NO_2\text{-}2)_2]$	D.r.	9·22	13·3 (sh)	15·62	15·22	26·6
$[Ni(quin)_2(O_2C\cdot C_6H_4NO_2\text{-}2)_2]$	D.r.	9·17		15·87		26·3

* D.r. = Diffuse reflectance, S. = solution. † Energies in 10^3 cm^{-1}; absorption coefficients (ε/l mol^{-1} cm^{-1}) are given in parentheses; sh = shoulder.

Spectra in solution were recorded in chloroform–amine solutions (10 : 1), the base being added to reduce the dissociation found in the molecular-weight studies. The spectra were generally similar to the diffuse-reflectance spectra, but the bands usually occurred at lower energy, indicating that some loss of base still occurs (Table 1). Among related studies Maggio *et al.*[11] only observed ν_2 and ν_3 of $[Ni(py)_2(O_2CMe)_2]$ at 16 250 and 26 150 cm^{-1}. Lever and Ogden [19] also found small falls in ν_2 and ν_3 of $[Ni(py)_2(O_2CCHCl_2)_2]$ in chloroform but did not see ν_1 in the diffuse-reflectance spectrum, and attributed a shoulder on ν_3 at 22 320 cm^{-1} to the transition to $^1T_{2g}$.

(b) *Polarized single-crystal electronic spectrum of* $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$. The crystal morphology is shown in Figure 2; the turquoise crystals had a well developed (010) face with the *a* and *b* axes lying along the short and long diagonals respectively. The determination [12] of the crystal structure of the complex showed that the N–Ni–N molecular axis is parallel to the *b* axis, the O–Ni–O (water) axis is roughly parallel to the *c* axis, and the O–Ni–O (acetate) axis is roughly parallel to the *a* axis. The polarized single-crystal electronic spectra were recorded along the *a*, *b*, and *c* crystallographic axes, and are shown in Figure 3. The spectra were recorded up to 24 000 cm^{-1}, so only ν_1 and

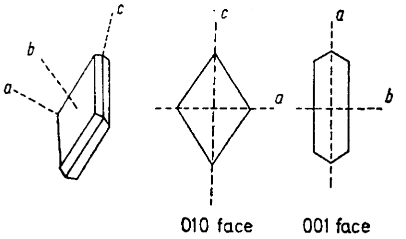

FIGURE 2 Crystal morphology of $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$

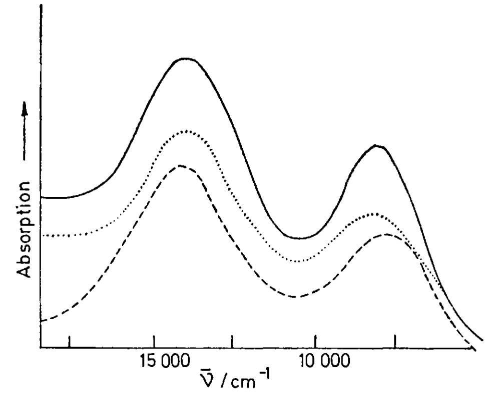

FIGURE 3 Polarized single-crystal electronic spectra of $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$ recorded along the *a* (· · · ·), *b* (——), and *c* crystallographic axes (— — —)

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[19] A. B. P. Lever and D. Ogden, *J. Chem. Soc.* (*A*), 1967, 2041.

ν_2 were observed. The spectra parallel to the *a* and *b* axes were similar, showing maxima at 10 000 and 16 000 cm^{-1}. The spectrum along the *c* axis differed in having ν_1 shifted to lower energy at 9 600 cm^{-1}.

The strict microsymmetry of the $NiN_2O_2(O')_2$ chromophore is D_{2h}, but the observed spectra indicate that a D_{4h} model should be applied, with the energy levels being those shown in Figure 1. As the molecule has a centre of symmetry, the most important mechanism for relaxing the parity selection rule is vibronic coupling. Thus for any transition to be allowed the direct product of the representations of the initial and final electronic states and that of the dipole-moment operator ($A_{2u} + E_u$ in D_{4h} symmetry) must include the representation of one of the odd normal modes of vibration, which are $2A_{2u} + B_{2u} + 3E_u$. Table 2 lists the direct products and gives the predicted band polarizations.

TABLE 2

Vibronic selection rules

Transition (from $^3B_{1g}$)	Direct product of electronic wave functions	Direct products with dipole-moment operators		Polarization
		xy	z	
$^3B_{2g}$	B_{2g}	E_u	B_{1u}	xy
^3E_g	E_g	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	E_u	$xy + z$
$^3A_{2g}$	B_{2g}	E_u	B_{1u}	xy

The spectra (Figure 3) show that the unique axis is the *c* axis, which gives the band at 9 600 cm^{-1} the assignment as the $^3B_{1g}\rightarrow{}^3E_g$ transition. Thus the O–Ni–O (water) axis is the principal axis of the molecule, and the tetragonal distortion involves weak axial bonds between nickel and water, not as possibly anticipated relatively strong bonds between nickel and py. The band at 10 000 cm^{-1} in the other directions then represents the unresolved pair of transitions to ^3E_g and $^3B_{2g}$, and as usual in tetragonal nickel(II) spectra no splitting is seen in ν_2. It is reasonable that there should be a tetragonal distortion along the O–Ni–O (water) axis since these oxygen atoms are each involved in one intramolecular and one intermolecular hydrogen bond,[12] and these will tend to pull the oxygen atoms away from the nickel ion. The Ni–O distance for the water oxygen is 2·102(5) Å, significantly longer than that of 2·505(5) Å for the co-ordinated acetate oxygen. Another example of hydrogen bonds affecting the donor power of a ligand was found in the nickel(II) complexes of a macrocyclic ligand[20] in which co-ordinated chloride and bromide showed anomalously lower ligand-field strengths because of their participation in hydrogen bonding with a water molecule.

TABLE 3

Electronic spectra at low temperature and ligand-field parameters

Complex	Transition (from $^3B_{1g}$)/10^3 cm^{-1}				Dt/cm^{-1}	$Dq(xy)$/cm^{-1}	$Dq(z)$/cm^{-1}
	$^3B_{2g}$	^3E_g	^1E_g	$^3T_{1g}(F)$			
$[Ni(py)_2(H_2O)_2(O_2CMe)_2]$	10·36	9·26	14·49 (sh)	16·80	+125	1 035	795
$[Ni(py)_2(O_2CMe)_2]$	9·61	9·95	13·60 (sh)	16·67	−40	960	1 030
$[Ni(py)_2(O_2CPh)_2]$	9·17	9·71	13·60 (sh)	16·40	−62	915	1 025
$[Ni(py)_2(O_2C{\cdot}C_6H_4Cl\text{-}4)_2]$	7·94	9·93	14·93 (sh)	16·95	−165	795	1 085
$[Ni(2\text{-}Mepy)_2(O_2CPh)_2]$	8·89			15·75			

(c) *Diffuse-reflectance spectra at low temperature.* The low-temperature diffuse-reflectance spectra of some of the complexes are listed in Table 3. Despite precautions, the formation of ice films gave poor results for the other complexes. The shifts in band frequencies at lower temperatures confirm the assignments of ν_1, ν_2, and the transition to ^1E_g, since the spin-allowed bands shifted to higher energy and the spin-forbidden band was almost unchanged, in accordance with the predictions of the Tanabe–Sugano diagram. Also the sharpening of the bands associated with the reduction in vibrations allows the spin-forbidden band to be observed in those py complexes in which it is obscured at room temperature. For most of the complexes, ν_1, but not ν_2, was resolved into two components. In the anhydrous py complexes the transition to $^3B_{2g}$ is assigned as the lower-energy component of ν_1 since these complexes represent two strong and four weak ligands rather than the two weak and four strong discussed for the single-crystal polarized spectrum of $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$. A shoulder at 20 200 cm^{-1} was observed for this complex at low temperature, and was assigned to the $^3B_{1g}\rightarrow{}^1T_{2g}$ transition.

The correlation diagram for the change in symmetry from O_h to D_{4h} (Figure 1) shows that the energies of the two components ν_B and ν_E of ν_1 can be related to the Dq values of the weak and strong ligands, $Dq(xy)$ and $Dq(z)$ respectively, and to the tetragonal-splitting parameter Dt by the equations (1)—(3).[2] The resulting

$$Dq(xy) = 1/10\ \nu_B \tag{1}$$

$$Dq(z) = 1/10\ (2\nu_E - \nu_B) \tag{2}$$

$$Dt = 4/35\ (\nu_B - \nu_E) \tag{3}$$

values of these parameters are given in Table 3. For $[Ni(py)_2(H_2O)_2(O_2CMe)_2]$ the Dq values compare reasonably with those of 850 cm^{-1} found[21] in $[Ni(H_2O)_6]^{2+}$ and of 1 015 cm^{-1} found[22] in $[Ni(py)_6]^{2+}$. The trend in the values of $Dq(xy)$ for the anhydrous complexes follows the order of pK_a values of the parent acids. Zink and Drago[8] did not establish a clear trend between pK values of the acids and the Dq values of the anions in the series *trans*-[Ni(*meso*-stilbenediamine)$_2$(O$_2$CR)$_2$], in which substitution in the 4-position made little difference to Dq. We were not able to carry out similar n.m.r.

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[20] G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 4830.

[21] O. Bistrup and C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

[22] C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

studies for those of our complexes which are soluble, probably because loss of amine gave too great line-broadening effects. No splitting of ν_1 was seen in $[Ni(2\text{-}Mepy)_2(O_2CPh)_2]$ at low temperature. This molecule was therefore assigned the *cis*-configuration, which has been confirmed by *X*-ray crystallographic studies,[23] as has the assignment of a *trans*-configuration to $[Ni(quin)_2(O_2CPh)_2]$.

No binuclear complexes of the type $[Ni_2L_2(O_2CR)_4]$ were characterized in this study. Heating a weighed sample of $[Ni(quin)_2(O_2C\cdot C_6H_4NO_2\text{-}2)_2]$ *in vacuo* over phosphorus pentaoxide at 80 °C produced a weight loss corresponding to loss of one quin group per nickel and a colour change from green to lemon-yellow. The i.r. spectrum of this product was very similar to that of the bis(quin) adduct. Its magnetic moment was *ca.* 2·5 B.M. at 298 K falling to *ca.* 1·5 B.M. at 98 K, but these values were not reproducible with different batches and continued heating at 80 °C led to decomposition of the yellow material. We are therefore unable to claim with confidence the characterization of a nickel analogue of $[Cu_2(H_2O)_2(O_2CMe)_4]$.

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[4/1267 *Received, 26th June,* 1974]

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[23] M. B. Hursthouse and D. B. New, unpublished work.