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Preparation, Properties and Crystal Structures of Nickel(II) Complexes with Acyclic Schiff Bases Derived from 2,6-Diformyl-4-chlorophenol and 1,5-Diamino-3-thiapentane or 3,3′-Diamino-*N*-methyl-dipropylamine

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Abstract

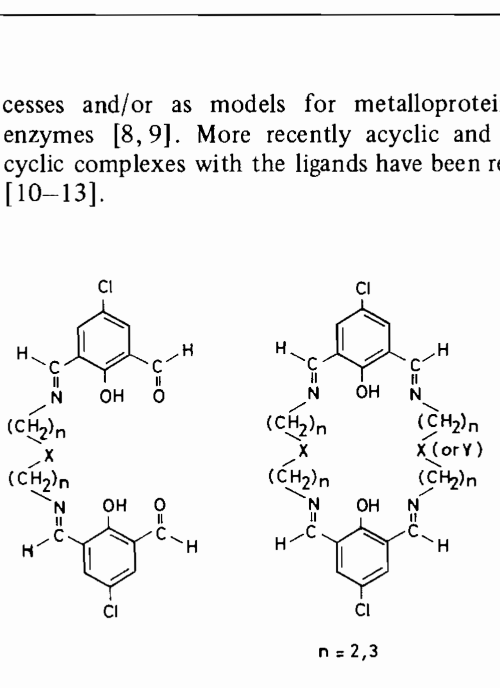
Nickel(II) complexes with the compartmental Schiff bases derived from 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-thiapentane (H_2L^1) or 3,3′-diamino-*N*-methyl-dipropylamine (H_2L^2) were synthesized, and the crystal structures of $[Ni(L^1)(py)_2]$ and $[Ni(L^2)(dmf)]\cdot H_2O$ were determined by X-ray crystallography.

$Ni(L^1)(py)_2$ is monoclinic, space group $C2/c$, with $a = 18.457(6)$, $b = 11.116(7)$, $c = 16.098(6)$ Å, and $\beta = 115.79(5)°$; $D_c = 1.49$ g cm^{-3} for $Z = 4$. The structure was refined to the final R of 6.9%. The molecule has C_2 symmetry. The nickel atom is six-coordinated octahedral. Selected bond lengths are: Ni–O 2.04(1) Å, Ni–N(L^1) 2.08(1) Å, Ni–N(py) 2.17(1) Å.

$[Ni(L^2)(dmf)]\cdot H_2O$ is monoclinic, space group $P2_1/n$, with $a = 17.329(6)$, $b = 13.322(7)$, $c = 12.476(7)$ Å and $\beta = 95.43(5)°$; $D_c = 1.45$ g cm^{-3} for $Z = 4$. The structure was refined to the final R of 5.1%. The nickel atom is bonded in the octahedral geometry to the bianionic pentadentate ligand L^2 and to one molecule of dimethylformamide. Selected bond lengths are: Ni–O (charged) 2.063(3) Å (mean value), Ni–O (neutral) 2.120(3) Å, Ni–N (planar) 2.050(3) Å (mean value), Ni–N (tetrahedral) 2.177(3) Å.

Introduction

Mononuclear and binuclear complexes of a series of Schiff bases derived from 2,6-diformyl-4-X-phenols (X = Cl, CH_3) and polyamines have been studied in detail in recent years [1–3]. Considerable interest has been shown in the magnetic exchange interaction between the metal ions [4–6], for the electrochemical behaviour of these systems [7], and for their possible application in oxidation processes and/or as models for metalloproteins and enzymes [8, 9]. More recently acyclic and macrocyclic complexes with the ligands have been reported [10–13].



n = 2,3

X, Y = NH, NCH_3, S

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In these complexes some doubts remained about the coordination of the X-donor atom to the central metal ion in the complexes. It was reported that the pentadentate Schiff base bis-salicylidene-1,5-diimino-3-azapentane is unable without strain to act in monomeric species as a quinquedentate ligand [14]. Thus, we prepared nickel(II) complexes with the acyclic ligands derived from 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-thiapentane (H_2L^1) or 3,3′-diamino-*N*-methyl-dipropylamine (H_2L_2), in order to have additional information about the influence of the aliphatic chain upon coordination of the central NH or NCH_3 groups to the metal, and we determined the structure of the complexes with H_2L^1 and H_2L^2.

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Experimental

$Ni(CH_3COO)_2 \cdot 4H_2O$, 1,5-diamino-3-thiapentane, 3,3'-diamino-*N*-methyl-dipropylamine and the solvents were commercial products (K & K) and were used without further purification. 2,6-diformyl-4-chlorophenol was prepared according to literature procedure [15]; its purity was checked by elemental analysis, melting point, IR, NMR and mass spectra.

Compounds

[Ni(L^1)(py)$_2$]

To a methanolic solution of 2,6-diformyl-4-chlorophenol (368 mg, 2 mmol) 1,5-diamino-3-thiapentane (120 mg, 1 mmol) was added. To the yellow suspension dissolved in $CHCl_3$, $Ni(CH_3COO)_2 \cdot 4H_2$ (248 mg, 1 mmol) in methanol was added and $Ni(L^1) \cdot MeOH$ was obtained as an orange-yellow precipitate. The product was filtered, washed with methanol and dried *in vacuo*. $Ni(L^1) \cdot MeOH$, obtained by this procedure, was dissolved in hot pyridine and the solution was slowly cooled until, after a few days, well formed crystals of $[Ni(L^1)(py)_2]$ were obtained. *Anal.* Calc. for $Ni(L^1) \cdot MeOH$: C, 46.32; H, 3.69; N, 5.16. Found: C, 46.22; H, 3.72; N, 5.28%. *Anal.* Calc. for $[Ni(L^1)(py)_2]$: C, 53.92; H, 3.89; N, 8.39. Found: C, 53.85; H, 3.95; N, 8.43%.

[Ni(L^2)(dmf)]·H$_2$O

To a pale yellow methanolic (50 ml) solution of 2,6-diformyl-4-chlorophenol (920 mg, 5 mmol), $Ni(CH_3COO)_2 \cdot H_2O$ (622 mg, 2.5 mmol) was added as a solid. To the resulting yellow solution 3,3'-diamino-*N*-methyl-dipropylamine in methanol (10 ml) was added dropwise. The brown-yellow solution obtained was stirred overnight; the solvent was partially evaporated and diethylether (15 ml) was added. $Ni(L^2) \cdot H_2O$ was obtained as a yellow precipitate; it was filtered and washed with ethanol and diethylether.

Crystals suitable for the X-ray analysis were grown from dimethylformamide. The crude product $Ni(L^2) \cdot H_2O$ was dissolved in dimethylformamide at 100 °C. The solution was slowly cooled until, after three

TABLE I. Crystal and Intensity Data

Compound	$[Ni(L^1)(py)_2]$	$[Ni(L^2)(dmf)]H_2O$
Formula	$C_{30}H_{26}Cl_2N_4O_4SNi$	$C_{26}H_{30}Cl_2N_4O_5Ni + H_2O$
Formula weight	667.7	607.92 + 18
System	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
General positions	$(000, 1/2, 1/2, 0) \pm(x, y, z; \bar{x}, y, 1/2 - z)$	$\pm(x, y, z; 1/2 + x, 1/2 - y, 1/2 + z)$
a (Å)	18.457(6)	17.329(6)
b (Å)	11.116(7)	13.322(7)
c (Å)	16.098(6)	12.476(7)
β (°)	115.79(5)	95.43(5)
V (Å^3)	2974	2867
Z	4	4
D_c (g cm^{-3})	1.49	1.45
Maximum crystal size (mm)	0.2	0.2
Radiation	Mo Kα	Mo Kα
μ(Mo Kα) (cm^{-1})	8.8	9.1
Technique and geometry	four-circle diffractometer (Philips PW 1100) with graphite-monochromated radiation; $\vartheta/2\vartheta$ scan mode; scan rate 2° min^{-1}	
ϑ_{max} (°)	25	25
Stability	no significant variation	no significant variation
Number of recorded reflections	4287	5515
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Number of observed reflections	1001	3765
Corrections applied	Lorentz polarization, absorption [20]	Lorentz polarization, absorption [20]
Atomic scattering factors	Ni: ref. 21; C, H, N, O, Cl, S: ref. 24	
Correction for anomalous dispersion (Ni)	$\Delta F' = 0.37$	$\Delta F'' = 1.20$
Solution	Patterson and Fourier methods	
Refinement method	Full-matrix least-squares	
Number of reflections per parameter refined	8.8	12.3
Conventional R factor	0.069	0.051
Weighting scheme (w)	1	1
Programs used	SHELX[23], PARST [24], PLUTO [25]	

TABLE II. Atomic Parameters for $[Ni(L^1)(py)_2]$

Atom	x/a	y/b	z/c
Atomic coordinates			
Ni1	1.00000(0)	0.49205(26)	0.25000(0)
S1	1.00000(0)	0.88729(54)	0.25000(0)
Cl1	0.56879(20)	0.59583(40)	0.09663(27)
O1	0.91390(42)	0.48810(86)	0.29723(48)
O2	0.76894(62)	0.38499(98)	0.41146(65)
N1	0.93134(56)	0.62357(99)	0.15750(63)
N2	0.93631(63)	0.35467(99)	0.14831(76)
C4	0.70105(37)	0.49471(77)	0.23818(48)
C5	0.67159(37)	0.55904(77)	0.15558(48)
C6	0.72432(37)	0.59978(77)	0.12060(48)
C7	0.80651(37)	0.57621(77)	0.16824(48)
C1	0.83598(37)	0.51188(77)	0.25084(48)
C2	0.78325(37)	0.47114(77)	0.28581(48)
C3	0.81031(78)	0.40834(122)	0.37180(87)
C8	0.85517(74)	0.63491(114)	0.12872(84)
C9	0.96668(71)	0.70520(136)	0.11214(88)
C10	1.01819(170)	0.79547(270)	0.16850(190)
C11	0.92769(80)	0.36630(131)	0.06323(93)
C12	0.88258(81)	0.28845(131)	−0.00677(100)
C13	0.84605(89)	0.19131(154)	0.01276(108)
C14	0.85568(89)	0.17891(155)	0.10020(105)
C15	0.90121(79)	0.26265(130)	0.16799(98)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters[a]						
Ni1	387(13)	529(20)	375(13)	340(41)	167(12)	183(55)
S1	1240(66)	514(47)	1561(78)	349(132)	1081(66)	554(100)
Cl1	405(19)	967(33)	773(27)	224(25)	190(19)	−37(22)
O1	485(46)	529(57)	463(45)	192(56)	232(38)	91(52)
O2	943(77)	934(87)	665(65)	264(63)	504(62)	−54(69)
N1	386(61)	611(77)	285(53)	−22(53)	154(48)	−189(55)
N2	509(34)					
C4	466(29)					
C5	473(34)					
C6	450(32)					
C7	436(32)					
C1	416(28)					
C2	404(30)					
C3	511(34)					
C8	460(33)					
C9	378(70)					
C10	1380(94)					
C11	585(39)					
C12	637(42)					
C13	764(46)					
C14	732(44)					
C15	593(39)					

[a] Anisotropic thermal parameters are in the form $T = \exp[-2\pi^2(U_{ij}h_ih_ja_i^*a_j^*)]$.

weeks, crystals of $[Ni(L^2)(dmf)]\cdot H_2O$ were obtained. *Anal.* Calc. for $Ni(L^2)\cdot H_2O$: C, 49.94; H, 4.52; N, 7.60. Found: C, 50.65; H, 4.32; N, 7.54%. *Anal.* Calc. for $[Ni(L^2)(dmf)]\cdot H_2O$: C, 49.86; H, 5.11; N, 8.95%. Found: C, 49.75; H, 5.21; N, 8.90%.

X-ray Data

Crystal and X-ray data for $[Ni(L^1)(py)_2]$ and $[Ni(L^2)(dmf)]\cdot H_2O$ are given in Table I. From the density value only four molecules of 1 are present in the unit cell, both the metal and the sulphur atoms must occupy special positions. Space group *C2/c* has four sets of special positions with point symmetry C_i-$\bar{1}$ and one set with point symmetry C_2-2. Because the molecule of the compound is acentric, Ni and S were located on the two fold axis at 0, *y*, 1/4; 0, $\bar{y}$, 3/4, where the *y* coordinates were determined from the Patterson peaks. In both compounds the phenylene rings were refined as rigid bodies C–C = 1.395 Å, C–H = 1.08 Å. The coordinates of the other hydrogen atoms in [Ni(L^2)(dmf)]·H$_2$O were derived from the electron density map. A final Fourier difference map showed no significant residuals. At convergence, the maximum shift on the refined parameters was 0.2σ for both compounds. Tables II and III list the above atomic positional parameters. Bond lengths and angles are given in Tables IV–VII.

Results and Discussion

Reaction of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-azapentane or 3,3′-diamino-*N*-methyldipropylamine in a 2:1 molar ratio with the appropriate metal acetate yields mononuclear acyclic complexes (Scheme 1) where the metal ion is coordinated in the inner N$_2$XO$_2$ chamber, the two formyl groups being not involved in the coordination. The usual equatorial

TABLE III. Atomic Parameters for [Ni(L^2)(dmf)]·H$_2$O

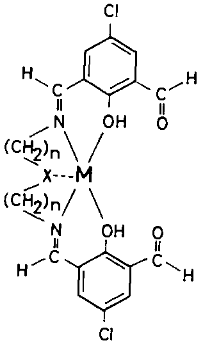
Atom	*x/a*	*y/b*	*z/c*
Atomic coordinates			
Ni1	0.48673(4)	0.76245(5)	0.28569(5)
Cl1	0.17550(12)	1.02104(17)	0.49275(23)
Cl2	0.15438(11)	0.52073(16)	0.46146(15)
O1	0.45190(20)	0.77944(29)	0.43868(27)
O2	0.37180(20)	0.75132(28)	0.22782(29)
O3	0.14947(26)	0.83627(36)	0.19237(45)
O4	0.30541(31)	0.67667(43)	0.64513(38)
O5	0.51304(24)	0.74001(36)	0.12465(30)
O6	0.01646(29)	0.71691(45)	0.15985(39)
N1	0.47736(27)	0.91566(34)	0.27299(36)
N2	0.61142(26)	0.77990(40)	0.32789(37)
N3	0.48410(29)	0.60907(35)	0.30423(38)
N4	0.46218(31)	0.72376(44)	−0.04699(38)
C1	0.38896(17)	0.83455(25)	0.44968(29)
C2	0.33699(17)	0.80274(25)	0.52149(29)
C3	0.27084(17)	0.85933(25)	0.53480(29)
C4	0.25667(17)	0.94774(25)	0.47632(29)
C5	0.30864(17)	0.97955(25)	0.40451(29)
C6	0.37479(17)	0.92296(25)	0.39119(29)
C7	0.42659(32)	0.96647(43)	0.31773(46)
C8	0.53036(36)	0.97329(52)	0.21057(52)
C9	0.61324(38)	0.96342(54)	0.26458(62)
C10	0.64727(37)	0.85734(56)	0.25978(58)
C11	0.65514(37)	0.68567(57)	0.30896(61)
C12	0.62498(38)	0.59022(58)	0.36076(61)
C13	0.55360(39)	0.54657(51)	0.29517(60)
C14	0.42375(36)	0.56145(45)	0.32934(49)
C15	0.34667(15)	0.60759(26)	0.33103(31)
C16	0.29430(15)	0.55291(26)	0.38618(31)
C17	0.21741(15)	0.58441(26)	0.38437(31)
C18	0.19290(15)	0.67058(26)	0.32742(31)
C19	0.24528(15)	0.72526(26)	0.27227(31)
C20	0.32217(15)	0.69377(26)	0.27408(31)
C21	0.46197(39)	0.75859(56)	0.05152(47)
C22	0.52324(55)	0.65416(72)	−0.07353(65)
C23	0.39758(45)	0.74757(74)	−0.13071(54)
C24	0.21828(36)	0.81124(48)	0.20888(55)
C25	0.34882(38)	0.70743(54)	0.57959(47)
C26	0.62446(36)	0.80915(58)	0.44384(48)

(continued)

TABLE III *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal Parameters[a]						
Ni1	363(3)	429(4)	326(3)	−19(3)	39(3)	14(3)
Cl1	583(11)	863(15)	1638(24)	−258(15)	426(13)	133(11)
Cl2	712(12)	873(14)	695(12)	127(10)	149(9)	−206(10)
O1	400(20)	503(23)	316(18)	28(17)	44(15)	−8(17)
O2	384(19)	441(22)	457(21)	9(18)	−26(16)	1(17)
O3	478(27)	592(29)	1109(41)	109(28)	−134(26)	24(22)
O4	871(37)	997(41)	599(31)	147(29)	241(27)	−190(32)
O5	547(24)	799(32)	339(21)	−88(22)	35(18)	60(24)
O6	730(33)	1158(46)	615(31)	35(31)	58(25)	−141(32)
N1	437(27)	428(26)	397(26)	31(21)	34(21)	−67(22)
N2	384(25)	643(33)	415(26)	−38(24)	76(20)	3(24)
N3	466(28)	451(27)	441(28)	−34(22)	−23(22)	103(24)
N4	643(33)	761(38)	348(26)	12(26)	32(23)	−93(30)
C1	393(12)					
C2	437(13)					
C3	547(16)					
C4	585(17)					
C5	516(15)					
C6	438(13)					
C7	402(31)	455(33)	456(33)	−38(27)	49(26)	−39(26)
C8	540(39)	649(42)	568(39)	117(33)	173(31)	−106(32)
C9	490(38)	647(45)	846(51)	85(39)	120(35)	−129(33)
C10	425(35)	776(49)	740(47)	110(39)	205(32)	−85(33)
C11	419(36)	758(48)	827(51)	16(40)	134(34)	154(34)
C12	450(38)	740(49)	829(51)	52(40)	−45(34)	148(35)
C13	510(38)	556(40)	822(49)	−29(36)	61(34)	162(32)
C14	490(36)	439(33)	523(36)	−28(28)	−38(28)	12(28)
C15	435(13)					
C16	482(14)					
C17	519(15)					
C18	496(14)					
C19	460(14)					
C20	403(12)					
C21	657(41)	749(47)	386(33)	−19(33)	48(29)	46(37)
C22	1088(69)	1066(69)	652(50)	−210(48)	223(47)	190(57)
C23	806(51)	1269(74)	456(38)	160(46)	−134(35)	−172(53)
C24	489(38)	487(36)	710(44)	−31(33)	−94(32)	50(30)
C25	656(41)	783(47)	346(32)	−4(31)	77(29)	−282(36)
C26	465(35)	950(53)	402(34)	−129(35)	−43(27)	−97(35)

[a] Anisotropic thermal parameters are in the form $T = \exp[-2\pi^2(U_{ij}h_ih_ja_i^*a_j^*)]$.



$n = 2$, X = NH; $n = 3$, X = N–CH_3; M = UO_2^{2+}, Cu^{2+}, Ni^{2+}
Scheme 1.

pentacoordination of UO_2^{2+} certainly involves the fifth nitrogen atom giving heptacoordinated uranium, while the nickel coordination mode to the same ligand could be hardly evaluated by physicochemical behaviour because solvent molecules (water or methanol) can be also coordinated to a greater or lesser extent. We were unable to grow crystals from water or methanol solutions, but the structural data obtained from the pyridine and the dimethylformamide complexes are referable to these other complexes.

As shown in Figs. 1 and 2 [Ni(L^1)(py)$_2$] and [Ni(L^2)(dmf)]·H_2O are six-coordinate monomeric complexes in which the metal atoms are in a slightly distorted octahedral environment. In [Ni(L^1)(py)$_2$]

TABLE IV. Bond Distances (Å) for $[\mathrm{Ni(L^1)(py)_2}]$

Ni–O(1)	2.039(7)	C(2)–C(3)	1.43(1)
Ni–N(1)	2.08(1)	C(9)–C(10)	1.41(2)
Ni–N(2)	2.17(1)	C(10)–S	1.81(2)
O(1)–C(13)	1.33(1)	N(2)–C(11)	1.32(2)
C(5)–Cl	1.76(1)	N(2)–C(15)	1.32(2)
C(7)–C(8)	1.46(1)	C(11)–C(12)	1.38(2)
N(1)–C(8)	1.28(1)	C(12)–C(13)	1.38(2)
N(1)–C(9)	1.48(1)	C(13)–C(14)	1.35(2)
		C(14)–C(15)	1.40(2)
		O(2)–C(3)	1.22(1)

TABLE V. Bond Angles (°) for $[\mathrm{Ni(L^1)(py)_2}]^a$

O(1)–Ni–O(1$^{\mathrm{I}}$)	177.2(4)	C(2)–C(3)–O(2)	125(1)
O(1)–Ni–N(1)	87.2(3)	C(7)–C(8)–N(1)	126(1)
N(1)–Ni–N(1$^{\mathrm{I}}$)	90.6(6)	C(8)–N(1)–C(9)	114(1)
O(1)–Ni–N(2)	90.7(4)	C(10)–S–C–C(10$^{\mathrm{I}}$)	112(1)
N(1)–Ni–N(2)	89.6(3)	C(11)–N(2)–C(15)	118(1)
Ni–O(1)–C(1)	128.0(5)	C(11)–C(12)–C(13)	119(1)
Ni–N(1)–C(8)	124.0(9)	C(12)–C(13)–C(14)	118(2)
Ni–N(1)–C(9)	121.5(7)	C(13)–C(4)–C(15)	120(2)
Ni–N(2)–C(11)	119.8(10)	C(14)–C(15)–N(2)	121(1)
Ni–N(2)–C(15)	121.6(9)	N(2)–C(11)–C(12)	123(1)

[a] Symmetry code: none, x, y, z; I, $2 - x, y, 0.5 - z$.

TABLE VI. Bond Distances (Å) for $[\mathrm{Ni(L^2)(dmf)}]\cdot\mathrm{H_2O}$

Ni–O(1)	2.067(3)	Ni–N(1)	2.043(4)
Ni–O(2)	2.059(3)	Ni–N(2)	2.177(4)
Ni–O(5)	2.120(3)	Ni–N(3)	2.056(4)
Cl(1)–C(4)	1.744(3)	Cl(2)–C(17)	1.752(3)
O(1)–C(1)	1.333(3)	O(2)–C(20)	1.313(4)
O(4)–C(25)	1.217(6)	O(3)–C(24)	1.226(6)
C(6)–C(7)	1.452(6)	C(15)–C(14)	1.461(5)
C(7)–N(1)	1.273(6)	C(14)–N(3)	1.274(6)
N(1)–C(8)	1.470(6)	N(3)–C(13)	1.467(6)
C(8)–C(9)	1.515(7)	C(13)–C(12)	1.510(7)
C(9)–C(10)	1.515(8)	C(12)–C(11)	1.511(8)
C(10–N(2)	1.495(6)	C(11)–N(2)	1.488(6)
N(2)–C(26)	1.479(6)	O(5)–C(2)	1.226(6)
N(4)–C(21)	1.311(6)	N(4)–C(22)	1.463(8)
		N(4)–C(23)	1.486(7)
Hydrogen bonds (Å)^a			
O(6)•••O(3)	2.798(4)		
O(6)•••O(1$^{\mathrm{I}}$)	2.871(4)		

[a] $I = 0.5 - x, 1.5 - y, 0.5 + z$.

TABLE VII. Bond Angles (°) $[\mathrm{Ni(L^2)(dmf)}]\cdot\mathrm{H_2O}$. Estimated Standard Deviations Refer to the Last Significant Digit

Angles involving Ni			
O(1)–Ni–O(5)	175.4(1)	O(2)–Ni–N(3)	86.4(1)
O(2)–Ni–N(2)	173.3(1)	N(2)–Ni–N(1)	88.9(2)
O(1)–Ni–N(3)	89.6(1)	N(2)–Ni–N(3)	96.2(2)
O(1)–Ni–O(2)	88.5(1)	Ni–O(1)–C(1)	117.7(2)
O(1)–Ni–N(1)	86.2(1)	Ni–O(2)–C(20)	122.6(2)
O(1)–Ni–N(2)	97.6(1)	Ni–O(5)–C(21)	118.6(3)
O(1)–Ni–N(3)	89.6(1)	Ni–N(1)–C(7)	122.6(3)
O(5)–Ni–O(2)	87.1(1)	Ni–N(1)–C(8)	120.5(3)
O(5)–Ni–N(1)	95.2(1)	Ni–N(2)–C(10)	113.0(3)
O(5)–Ni–N(2)	86.9(1)	Ni–N(2)–C(11)	112.4(3)
O(5)–Ni–N(3)	88.7(2)	Ni–N(2)–C(26)	109.1(3)
O(2)–Ni–N(1)	88.9(1)	Ni–N(3)–C(13)	121.2(3)
		Ni–N(3)–C(14)	121.9(3)
Angles involving L^2			
C(2)–C(25)–O(4)	125.5(5)	C(19)–C(24)–O(3)	126.2(5)
C(6)–C(7)–N(1)	124.6(4)	C(15)–C(14)–N(3)	125.7(4)
C(7)–N(1)–C(8)	116.9(4)	C(14)–N(3)–C(13)	116.9(4)
N(1)–C(8)–C(9)	109.6(4)	N(3)–C(13)–C(12)	112.8(4)
C(8)–C(9)–C(10)	114.8(5)	C(13)–C(12)–C(11)	113.7(5)
C(9)–C(10)–N(2)	116.7(4)	C(12)–C(11)–N(2)	116.3(4)
C(10)–N(2)–C(26)	108.5(4)	C(11)–N(2)–C(26)	108.7(4)
		C(10)–N(2)–C(11)	104.9(4)
Angles involving dmf			
O(5)–C(21)–N(4)	125.2(5)	C(21)–N(4)–C(23)	121.1(5)
C(21)–N(4)–C(22)	119.4(5)	C(22)–N(4)–C(23)	119.2(5)

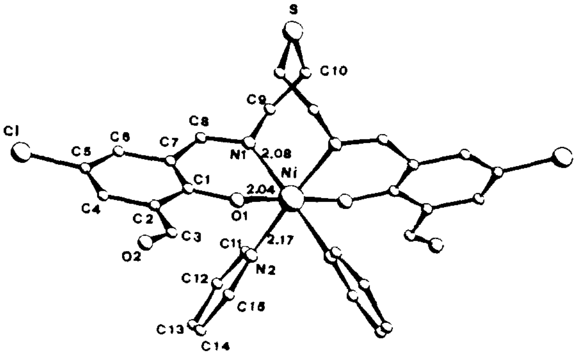


Fig. 1. The crystal structure of $[\mathrm{Ni(L^1)(py)_2}]$.

both the Ni and S atoms lie on the crystallographic two fold axis so that the molecule as a whole has the C_2 symmetry. Coordination bond distances with the donor atoms of the chelate ligand compare well themselves, irrespective of the nature of the coordinated atoms, and are in the range of values generally expected for octahedral nickel complexes, whereas bonding to pyridines appears to be weaker and causes distortion of the octahedral environment.

It is useful to remember that, as demonstrated by the well-known structures of the Lifschitz nickel(II) complexes [16] and by other works [17–19], the observed Ni–N bond distances in octahedral paramagnetic molecules are significantly longer than the corresponding distances in square-planar diamagnetic molecules. The N(1)–C(8) bond (1.28(1) Å) is essentially double, and O(1)–C(1) is partial double with a value (1.33(1) Å) near to that of the longer bond in carboxylic acids and esters.

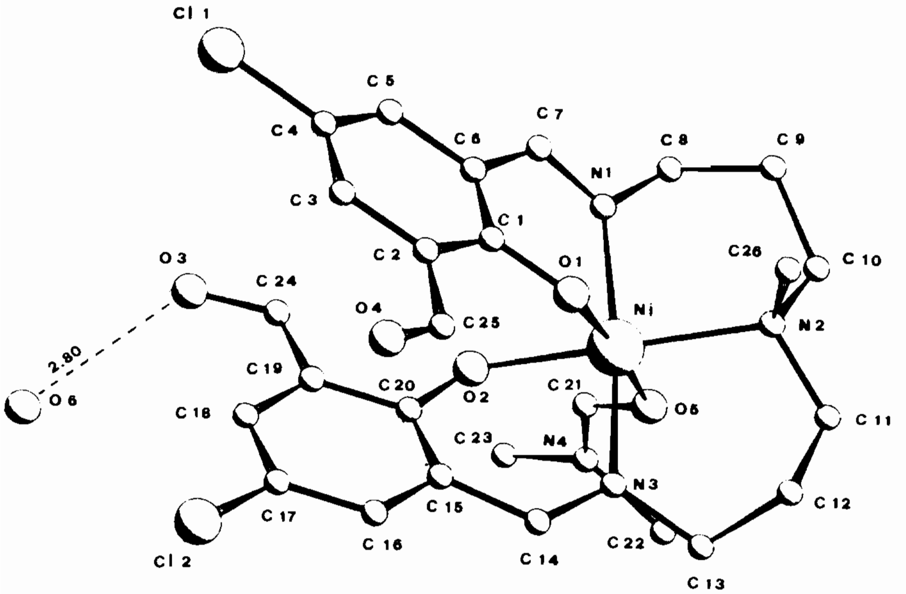


Fig. 2. The crystal structure of $[Ni(L^2)(dmf)] \cdot H_2O$.

As shown in Table I, refinement of $[Ni(L^2)(dmf)] \cdot H_2O$ is based on a greater number of observed reflections and structural details concerning this compound are therefore more accurate if compared with those of $[Ni(L^1)(py)_2]$ (see for this the e.s.d. values on bond distances and angles in the two compounds). Ni–O (charged) bond distances agree well themselves and are shorter than Ni–O (neutral) by *ca.* 0.06 Å. The nickel–nitrogen bonds are of two types: the *trans* Ni–N (planar) bonds are fully equivalent with a mean value of 2.050(3) Å, which is significantly shorter than the Ni–N (tetrahedral) bond of 2.177(3) Å. The relative weakness of the Ni–N(2) bond could be in part attributed to the different hybridization state of the nitrogen atom and, more likely, to the *trans* influence of the Ni–O(2) bond with the charged oxygen atom.

The O(1)–C(1) and O(2)–C(20) bonds (mean 1.323(4) Å) are partial double, as the longer bond in carboxylic acids and esters, whereas O(3)–C(4), O(4)–C(25), and O(5)–C(21) are double (mean 1.222(6) Å) as expected for aldehydes. All angles at N(2), which is tetrahedral, are all in the range 104.9–113.0°, showing that the pentadentate ligand is flexible enough to allow the lone pair of this atom to point directly toward the metal.

The N(1) and N(3) atoms are fully equivalent and make one single and one double C–N bond (mean for single 1.469(6) Å, mean for double 1.273(6) Å). The structure contains one molecule of crystallized water which provides hydrogen linking between adjacent molecules of the compound (see Table VI for hydrogen bonds).

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