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Five- and Six-Coordinate Nickel(II) Complexes of New Multidentate Ligands Containing 2,9-Disubstituted-1,10-Phenanthroline and Pyrazolyl Units

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The synthesis of the novel tridentate nitrogen ligand (2-((3,5-dimethyl-*N*-pyrazolyl)methyl)-1,10-phenanthrolin-9-yl)methyl ethyl ether (dpmp), $C_{21}H_{22}N_4O$, and of its dichloronickel(II) complex are reported. The structure of the nickel(II) complex and that of the *trans*-diaquanickel(II) complex of the related tetradentate ligand 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp), $C_{20}H_{16}N_6$, have been determined by three-dimensional X-ray diffraction methods. The chloride salt of the bpmp complex, $[Ni(bpmp)(OH_2)_2]Cl_2 \cdot H_2O$, crystallizes in space group $P\bar{1}$ of the triclinic system with two molecules in a cell of dimensions $a = 8.016(2)$ Å, $b = 9.997(2)$ Å, $c = 15.015(3)$ Å, $\alpha = 101.22(3)°$, $\beta = 92.50(3)°$, and $\gamma = 111.20(3)°$. The structure has been refined to a final value of the crystallographic R factor of 0.0272 based on 3861 observed independent reflections. The geometry at nickel is six-coordinate, pseudooctahedral, with water ligands *trans*. The dpmp complex $[Ni(dpmp)Cl_2] \cdot CH_3CN$ also crystallizes in space group $P\bar{1}$ of the triclinic system with two molecules in a cell of dimensions $a = 8.478(2)$ Å, $b = 9.644(2)$ Å, $c = 15.747(3)$ Å, $\alpha = 80.52(3)°$, $\beta = 84.58(3)°$, and $\gamma = 70.46(3)°$. The structure has been refined to a final value of the crystallographic R factor of 0.0652 based on 1655 observed independent reflections. The complex adopts a five-coordinate geometry, the coordination being provided by the two phen nitrogen atoms [N(1) and N(2)] and one pyrazole nitrogen atom [N(3)] from the ligand and by two chloride ions. The geometry at nickel is trigonal bipyramidal, with one phenanthroline and one pyrazolyl nitrogen atom axial while the other phenanthroline nitrogen atom and the chloride ligands are equatorial. The nickel(II) bpmp complex exhibits an irreversible reduction wave at −0.46 V *vs* Ag/AgCl; the nickel(II) dpmp complex, however, shows a quasi-reversible wave at $E_{1/2} = -0.61$ V, attributable to the Ni(II) ↔ Ni(I) couple.

Introduction

Novel ligands containing the 1,10-phenanthroline (phen) and pyrazolyl subunits have been synthesized. While the former unit has strong π-accepting ability and consequently provides a soft site for metal coordination, the latter unit is a better π donor and acts as a hard donor site. Hence, owing to the presence of this combination of soft and hard sites in a single ligand system, a fine tuning of the physical and chemical properties of the metal complexes of such ligands might be attainable. Moreover, if these ligands possess conformational flexibility, for instance by having methylene or ethylene bridges between the pyrazolyl and phenanthroline moieties, they could permit several different coordination modes. Consequently, we have undertaken a comprehensive effort to synthesize such flexible ligands and to study the different coordination modes available to metals, hoping eventually to design specific systems by a fine tuning of ligand properties. In the case of the nickel(II) complexes discussed in the present paper, further impetus to this work is provided by the observation that the nickel(II) complexes of 2,9-disubstituted phen ligands cited in the literature are either tetrahedral or pseudotetrahedral owing to the steric hindrance imposed by the 2,9-disubstitution at the phen;[1–3] we anticipated that our more flexible ligands would allow other geometries. Here we report the synthesis of the new ligand (2-((3,5-dimethyl-*N*-pyrazolyl)methyl)-1,10-phenanthrolin-9-yl)methyl ethyl ether (dpmp) and the isolation and characterization of its nickel(II) complex. We also report the preparation, properties, and crystal structure of a nickel(II) complex of the ligand 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp), whose synthesis and structural characterization we have reported previously.[4]

Experimental Section

Syntheses. All starting materials were purchased from Aldrich; whenever required, solvents were distilled and dried according to standard laboratory procedures. The C, H, and N analyses were carried out by Atlantic Microlab, Inc. The ligand 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp) was synthesized as reported previously.[4]

(2-((3,5-Dimethyl-*N*-pyrazolyl)methyl)-1,10-phenanthrolin-9-yl)methyl Ethyl Ether (dpmp). 2,9-Bis(bromomethyl)-1,10-phenanthroline (560 mg, 1.53 mmol)[4,5] was dissolved in ethanol (10 mL). Dichloromethane (25 mL) and then benzene (200 mL) were added. To this solution was added a 40% solution of NaOH (20 mL). The yellow solution immediately became much paler. Then 600 mg of 3,5-dimethylpyrazole (8.8 mmol) was added, followed by the addition of 40% tetrabutylammonium hydroxide (TBAH) solution (0.25 mL). After being refluxed for 36 h, the solution was cooled and the organic fraction was collected and dried over 2 g of anhydrous $MgSO_4$. It was then filtered, and the solvent was removed by rotary evaporation. Column chromatography on silica gel, first eluting with 1:1 v/v hexane–CH_2Cl_2 followed by 9:1 v/v CH_2Cl_2–$CH_3COOC_2H_5$ and then with 3.5:2 v/v CH_2Cl_2–$CH_3COOC_2H_5$ gave a first pale yellow fraction (tlc single spot, r_f 0.48). The elution continued to give a second fraction (tlc single spot, r_f 0.29), which is the desired material. The solvent was removed by rotary evaporation to give 200 mg of white to yellowish white solid, mp 153–155 °C. ^{1}H NMR ($CDCl_3$): t (3H, methyl), 1.25–1.40 ppm; twinned doublet (6H, pyrazolylmethyls), 2.10–2.35 ppm; q (2H, $-O-CH_2-$), 3.70–3.85 ppm; s (2H, $-CH_2-O-$) 5.1 ppm; s (2H, $-CH_2-N-$) 5.85 ppm; s (1H, pyrazolyl ring proton) 5.95 ppm; (6H, phen protons) 6.95–8.35 ppm. ^{13}C NMR ($CDCl_3$): 11.6, 13.9, 15.7, 55.6, 67.0, 74.6, 106.4, 120.6, 121.3, 126.3, 126.7, 128.2, 128.5, 137.3, 137.8, 140.4, 145.7, 145.8, 148.6, 158.8, 160.5 ppm. Anal. Calcd for $C_{21}H_{22}N_4O$: C, 72.83; H, 6.36, N, 16.18. Found: C, 72.44; H, 6.47; N, 15.79. IR (KBr pellet): 3193, 3134, 3108, 3032, 2973, 2923, 2855, 1707, 1589, 1547, 1497, 1437, 1412, 1378, 1294, 1116, 1091, 1024,

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Table 1. Crystallographic Details for the Structures

	$[Ni(bpmp)(H_2O)_2]Cl_2{\cdot}H_2O$	$[Ni(dpmp)Cl_2]{\cdot}CH_3CN$
formula	$C_{20}H_{22}Cl_2N_6NiO_3$	$C_{23}H_{25}Cl_2N_5NiO$
fw	524	517
a, Å	8.016(2)	8.478(2)
b, Å	9.997(2)	9.644(2)
c, Å	15.015(3)	15.747(3)
α, deg	101.22(3)	80.52(3)
β, deg	92.50(3)	84.58(3)
γ, deg	111.20(3)	70.46(3)
V, Å^3	1091.9(4)	1195.7(4)
Z	2	2
ρ_{calcd}, g cm^{-3}	1.594	1.436
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, K	295	295
λ, Å	0.710 69	0.710 69
μ, mm^{-1}	1.170	1.060
NO[a]	5020	4216
NO [$I > 3\sigma(I)$]	3861	1697
R[b]	0.0272	0.0752
R_w[c]	0.0423	0.0932

[a] NO = number of observed reflections. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

846, 796, 728, 703, 627 cm^{-1}. Mass spectrum: m/z = 347, 319, 303, 297, 207, 179, etc.

$[Ni(bpmp)(H_2O)_2]Cl_2{\cdot}H_2O$. A solution containing 0.5 mmol of nickel(II) chloride hexahydrate dissolved in methanol (10 mL) was added dropwise to a stirring solution containing 0.52 mmol of ligand dissolved in dichloromethane–methanol (10 mL, 1:1 v/v). The light green solution that resulted was allowed to stir for 30 min, and then the volume of the solution was reduced at room temperature to give a light green solid which was recrystallized from CH_3CN by slow passage of ether vapors into the solution to give beautiful purple violet rectangular crystals in 80% yield. Anal. Calcd for $NiC_{20}H_{22}N_6Cl_2O_3$: C, 45.83; H, 4.20; N, 16.04. Found: C, 45.81; H, 4.23; N, 16.24.

$[Ni(DPMP)Cl_2]$. A similar procedure was adopted as above to give a light green solid which was recrystallized from methanol. Anal. Calcd for Ni $C_{21}H_{22}N_4Cl_2O$: C, 52.97; H, 4.63; N, 11.77. Found: C, 52.86; H, 4.59; N, 11.84.

Physical Measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1600 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL 270 spectrometer; chemical shifts are listed in ppm relative to tetramethylsilane. Electronic spectra were obtained by using 1 × 10^{-3} M solutions in acetonitrile on a Perkin-Elmer Lambda 9 spectrometer. Cyclic voltammograms were obtained with a BAS 100A electrochemical analyzer. A three-electrode cell comprising a glassy-carbon or Pt-button working electrode, a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode was used. Solutions of nickel(II) complexes (1 × 10^{-3} M) in acetonitrile were used. The supporting electrolyte was 0.1 M tetraethylammonium perchlorate. All experiments were performed under a blanket of dry nitrogen at 22 ± 1 °C. All potentials are relative to Ag/AgCl.

X-ray Crystallography. X-ray quality crystals of $[Ni(bpmp)(H_2O)_2]Cl_2{\cdot}H_2O$ were grown from methanol–acetonitrile solutions to give beautiful purple-violet crystals, while for $[Ni(dpmp)Cl_2]$ fragile green needles were obtained when grown from acetonitrile solution. The structures of the complexes were determined at 22 °C (295 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1)$ = 0.709 26 Å; $\lambda(K\alpha_2)$ = 0.713 54 Å] and graphite monochromator. The structures were solved by direct methods and refined by least squares techniques, the programs being from the SHELXTL IRIS system. The data were corrected for Lorentz–polarization and for absorption effects. Crystallographic details and cell constants for both compounds are found in Table 1.

For the Ni(II)–bpmp complex, a crystal of dimensions 1.00 × 0.36 × 0.34 mm^3 was mounted. Data with $4 \leq 2\theta \leq 55°$ were collected in the range $0 \leq h \leq 10, -12 \leq k \leq 12, -19 \leq l \leq 19$. All hydrogen atoms were located, including those associated with the water molecules. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Final values of the conventional *R* factors were R = 0.0272 and R_w = 0.0423 based on 3861 independent data with $F \geq 6\sigma(F)$. Final atomic positional parameters and their estimated standard deviations are presented in Table 2.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $C_{20}H_{22}Cl_2N_6NiO_3$

	x	*y*	*z*	*U*(eq)[a]
Ni(1)	1476(1)	8816(1)	7124(1)	26(1)
N(1)	1413(2)	7609(2)	8102(1)	30(1)
N(2)	2395(2)	10519(2)	8277(1)	31(1)
N(3)	2127(2)	10282(2)	6293(1)	33(1)
N(4)	82(2)	6912(2)	6159(1)	32(1)
O(1W)	4033(2)	8718(2)	6923(1)	44(1)
O(2W)	−1042(2)	8945(2)	7323(1)	45(1)
N(5)	−415(2)	5569(2)	6362(1)	31(1)
N(6)	2907(2)	11760(2)	6655(1)	32(1)
C(1)	1026(3)	6181(2)	7988(1)	32(1)
C(2)	1136(3)	5537(3)	8731(2)	41(1)
C(3)	1673(3)	6391(3)	9596(2)	46(1)
C(4)	2109(3)	7915(3)	9738(1)	44(1)
C(5)	2673(4)	8907(3)	10618(2)	58(1)
C(6)	3071(4)	10352(3)	10712(2)	60(1)
C(7)	2964(3)	10959(3)	9930(2)	47(1)
C(8)	3381(4)	12474(3)	9979(2)	52(1)
C(9)	3287(3)	12948(2)	9201(2)	47(1)
C(10)	2767(3)	11935(2)	8344(1)	34(1)
C(11)	2466(3)	10024(2)	9055(1)	36(1)
C(12)	1967(3)	8474(2)	8962(1)	34(1)
C(13)	655(3)	5244(2)	7032(1)	33(1)
C(14)	−1820(3)	4568(2)	5770(1)	36(1)
C(15)	−2292(3)	5276(2)	5170(1)	40(1)
C(16)	−1088(3)	6725(2)	5440(1)	38(1)
C(17)	2655(3)	10103(2)	5459(1)	39(1)
C(18)	3737(3)	11436(3)	5286(2)	43(1)
C(19)	3864(3)	12469(2)	6058(2)	39(1)
C(20)	2444(3)	12447(2)	7504(1)	35(1)
O(3W)	6894(3)	4198(2)	8274(2)	74(1)
Cl(1)	−4588(1)	6290(1)	7341(1)	47(1)
Cl(2)	−2393(1)	11452(1)	6991(1)	45(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

For the Ni(II)–dpmp complex, a crystal of dimensions 1.10 × 0.21 × 0.22 mm^3 was used for data collection. Data with $4 \leq 2\theta \leq 50°$ were collected in the range $0 \leq h \leq 10, -11 \leq k \leq 11, -18 \leq l \leq 18$. In a late stage of the refinement it became apparent that the ether carbon atoms C(20) and C(21) were disordered, and these atoms were treated by the free variable method and refined isotropically; hydrogen atoms associated with these two carbon atoms were not included in the refinement. All other hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å) while other atoms were refined anisotropically. The final values of the conventional *R* factors were R = 0.0652 and R_w = 0.0773 based on 1655 independent data with $F \geq 8\sigma(F)$. Final atomic positional parameters and estimated standard deviations are presented in Table 3.

Results and Discussion

We have earlier reported the synthesis of the bpmp ligand.[4] This ligand was found to occupy four sites of a distorted trigonal bipyramid in a Cu(II) complex by adopting a very different conformation than that found in the free ligand.[4] Moreover, the combination of the π donor pyrazole rings and the π deficient phen moieties was found to lead to unusual electrochemical and structural properties. For example, the Cu(II) ↔ Cu(I) couple was found to be at $E_{1/2}$ = 0.037 V, which is higher than in the phen systems. In a continued effort to extend the range of these phen and pyrazolyl based ligands, we set out to synthesize the potentially tetradentate ligand 2,9-bis(3,5-dimethyl-*N*-pyrazolylmethyl)-1,10-phenanthroline, which is the 3,5-dimethylpyrazolyl analogue of bpmp. While preserving the electronic features of bpmp, the methyl groups of this new ligand would also provide significant steric constraints at the metal, and consequently might be expected to help in stabilizing lower oxidation state complexes. It is noteworthy in this context that, with the unconstrained bpmp ligand, we were unable to isolate the pure copper(I) complex. In fact, for the reasons discussed below, we actually formed the potentially tridentate ligand dpmp.

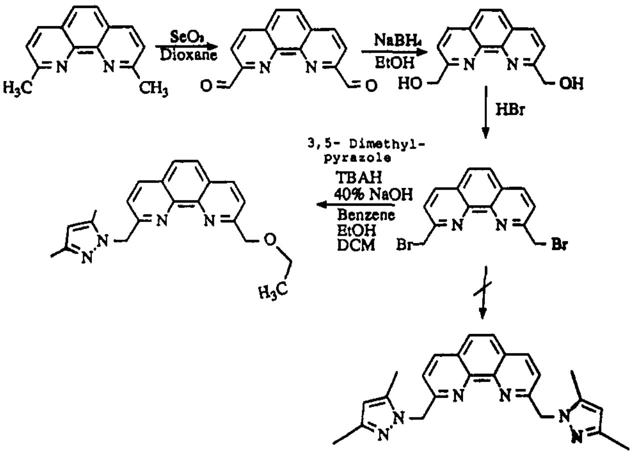
The synthetic strategy for the dpmp ligand is outlined in Scheme 1. It involves the oxidation of 2,9-dimethyl-1,10-phenanthroline to the corresponding dialdehyde, reduction of the dialdehyde to

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $C_{23}H_{25}N_5Cl_2NiO$

	x	*y*	*z*	*U*(eq)[a]
Ni(1)	1210(2)	2520(2)	2807(1)	40(1)
Cl(1)	-34(4)	4848(3)	2087(2)	65(1)
Cl(2)	3797(3)	647(3)	3031(2)	53(1)
N(1)	-531(11)	2071(8)	3674(5)	38(3)
N(2)	1765(12)	3326(10)	3878(7)	51(4)
N(3)	606(11)	1401(10)	1931(6)	46(4)
C(1)	-1762(13)	1579(11)	3557(8)	42(4)
C(2)	-2751(15)	1190(12)	4221(9)	55(5)
C(3)	-2504(16)	1270(12)	5061(9)	59(5)
C(4)	-1223(15)	1803(11)	5209(8)	50(5)
C(5)	-892(18)	1987(13)	6041(8)	64(6)
C(6)	260(19)	2619(14)	6127(8)	62(6)
C(7)	1200(17)	3115(12)	5432(8)	56(5)
C(8)	2399(24)	3860(15)	5454(13)	89(8)
C(9)	3161(19)	4294(15)	4735(12)	72(7)
C(10)	2842(15)	4013(12)	3935(9)	52(5)
C(11)	959(15)	2878(11)	4597(8)	46(4)
C(12)	-292(14)	2210(11)	4503(8)	48(5)
C(13)	-2111(13)	1588(13)	2632(7)	51(5)
C(14)	-616(16)	-132(13)	1562(8)	57(5)
C(15)	791(17)	-228(16)	1048(9)	71(6)
C(16)	1497(17)	774(15)	1275(9)	63(6)
C(17)	-1903(20)	-871(16)	1587(10)	80(7)
C(18)	3053(18)	1116(21)	911(10)	94(9)
C(19)	3610(16)	4520(14)	3122(11)	72(7)
O(1)	4685(16)	5257(15)	3240(9)	117(7)
C(20A)	5484(57)	5754(57)	2548(30)	116(7)
C(20B)	4748(76)	6709(68)	2561(38)	116(7)
C(21A)	4428(61)	6974(53)	1974(30)	116(7)
C(21B)	5215(74)	6150(64)	1766(36)	116(7)
N(4)	-676(11)	858(10)	2104(6)	42(4)
C(22)	8112(27)	4331(24)	94(13)	131(14)
C(23)	7023(27)	3473(22)	344(12)	94(9)
N(5)	6126(27)	2835(20)	557(14)	137(11)

[a] Equivalent isotropuc *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme 1



the diol, and bromination followed by phase transfer reaction. We have to use ethanol as one of the constituent solvents because of the very low solubility of the dibromide in benzene and dichloromethane. The reaction mixture gives two products, one of which was an intractable oily solid ($r_f = 0.48$) while the other ($r_f = 0.29$) is found to be the dpmp ligand, rather than the anticipated 2,9-bis(3,5-dimethyl-*N*-pyrazolylmethyl)-1,10-phenanthroline. The reaction was repeated under a variety of conditions, and at each time we generated the same two fractions in similar yields. Thus, it would appear that once the 3,5-dimethylpyrazolyl moiety is incorporated on one side of the phen system, it sterically inhibits the approach of another pyrazolyl unit; consequently, in the presence of ethanol, ethoxide ion finds easy access and becomes a hanging pendant group. Presumably, if we replaced ethanol by methanol, we would generate the methoxide analogue. In our earlier synthesis using the less hindered pyrazolyl system, we readily obtained the bpmp ligand in which two pyrazolyl rings were able to bind to the phen moiety.[4]

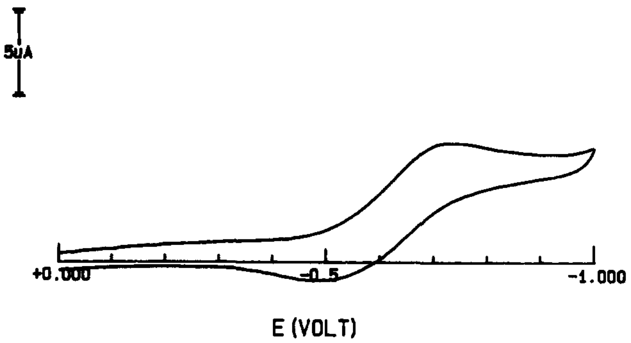


Figure 1. Cyclic voltammogram for [Ni(dpmp)Cl_2] in acetonitrile with 0.1 M TEAP as supporting electrolyte, scan rate 100 mV/s.

Complex Syntheses. We have chosen the nickel(II) ion for coordination studies in part because all the monomeric complexes of Ni(II) with 2,9-disubstituted phen cited in literature are either tetrahedral or pseudotetrahedral;[2,3] in addition, presumably to avoid steric interactions, dinuclear square pyramidal complexes are found.[6] In contrast, of course, octahedral or pseudooctahedral six-coordinate complexes $M(phen)_3$ result from the use of unsubstituted phen ligands.[1] The nickel(II) complexes with either dpmp or bpmp ligands were readily prepared as neutral complexes [$NiLX_2$] or as halide salts of diaqua complex cations [Ni(L)$(OH_2)_2]^{2+}$.

Electronic Absorption Spectra. The visible spectrum of [Ni(bpmp)$(H_2O)_2]^{2+}$ showed a broad band centered at 794 nm, ϵ = 10 M^{-1} cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$ in O_h symmetry), a band at 571 nm, ϵ = 18 M^{-1} cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}$), a weak hump at 329 nm, ($^3A_{2g} \rightarrow {}^3T_{1g}$(P)) with intraligand bands at 297 nm, log ϵ = 4.35, and 283 nm, log ϵ = 4.55. These observations are consistent with octahedral geometry for the complex, the intraligand bands being due to $\pi \rightarrow \pi^*$ transitions in the coordinated ligand.

The visible spectrum of [Ni(dpmp)Cl_2] exhibited a broad band from 1387 to 972 nm centered at 1170 nm, ϵ = 27 M^{-1} cm^{-1} ($^3E' \rightarrow {}^3A_1'' + {}^3A_2''$ in D_{3h} symmetry), another band at 673 nm, ϵ = 63 M^{-1} cm^{-1} ($^3E' \rightarrow {}^3A_2''$), and an intense band at 398 nm, ϵ = 222 M^{-1} cm^{-1}, corresponding to transitions from the ^3F to the ^3P manifold ($^3E''$ and $^3A_2'$), with intraligand band at 297 nm, log ϵ = 4.44, with a shoulder at 297 nm, log ϵ = 4.1, consistent with coordinated ligand. These bands suggest that the geometry around the nickel(II) ion must either be trigonal bipyramidal or distorted trigonal bipyramidal. A square pyramidal geometry can be discounted on the basis of the absence of $^3B_1 \rightarrow {}^3E$ and $^3B_1 \rightarrow {}^3A_2$ transitions usually found in the 2500–1110- and 400–588-nm regions.[7]

Electrochemistry. Redox processes were investigated by cyclic voltammetry in acetonitrile. The ligands are found to be electrochemically inactive in the working range. The cyclic voltammogram with carbon black working electrode for the nickel(II)–bpmp complex exhibited an irreversible reduction wave at –0.46 V. No other peaks could be observed, suggesting that the nickel(II) oxidation state in this complex is stable. As is shown in Figure 1, the cyclic voltammogram with Pt-button working electrode for the Ni(II)–dpmp complex exhibited a very broad, quasi-reversible peak with reduction wave at –0.72 V and an oxidation wave –0.49 V at a scan rate of 100 mV/s. The quasi-reversibility of the wave indicates that in this complex it is possible to form the Ni(I) oxidation state. The quasi-reversibility could also be an indication that significant structural changes could be occurring on changing from one oxidation state to other.

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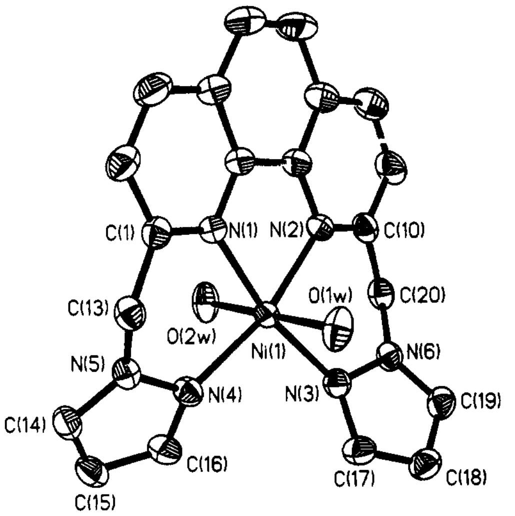

Figure 2. View of the structure of the cation $[Ni(bpmp)(H_2O)_2]^{2+}$ in the crystals of the chloride salt. Hydrogen atoms are omitted for clarity. Unlabeled carbon atoms in the phenanthroline rings are numbered in the standard manner [C(2)–C(12)].

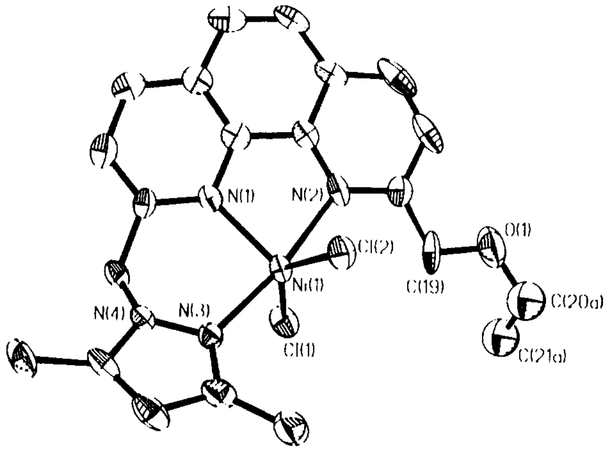

Figure 3. View of the structure of the neutral complex $[Ni(dpmp)Cl_2]$. Hydrogen atoms are omitted for clarity. Unlabeled carbon atoms in the phenanthroline rings are numbered in the standard manner [C(2)–C(12)]; unlabeled carbon atoms in the pyrazole ring are numbered C(14)–C(16), while methyl carbon atoms are C(17) and C(18).

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $C_{20}H_{22}Cl_2N_6NiO_3$

Bond Lengths

Ni(1)–N(1)	2.065(2)	Ni(1)–N(2)	2.067(1)
Ni(1)–N(3)	2.048(2)	Ni(1)–N(4)	2.054(1)
Ni(1)–O(1W)	2.119(2)	Ni(1)–O(2W)	2.099(2)

Bond Angles

N(1)–Ni(1)–N(2)	80.8(1)	N(1)–Ni(1)–N(3)	167.0(1)
N(2)–Ni(1)–N(3)	91.0(1)	N(1)–Ni(1)–N(4)	90.3(1)
N(2)–Ni(1)–N(4)	166.3(1)	N(3)–Ni(1)–N(4)	99.4(1)
N(1)–Ni(1)–O(1W)	86.3(1)	N(2)–Ni(1)–O(1W)	95.6(1)
N(3)–Ni(1)–O(1W)	84.5(1)	N(4)–Ni(1)–O(1W)	94.2(1)
N(1)–Ni(1)–O(2W)	94.4(1)	N(2)–Ni(1)–O(2W)	83.9(1)
N(3)–Ni(1)–O(2W)	94.8(1)	N(4)–Ni(1)–O(2W)	86.3(1)
O(1W)–Ni(1)–O(2W)	179.1(1)		

X-ray Crystal Structures. $[Ni(bpmp)(H_2O)_2]Cl_2{\cdot}H_2O$. The structure consists of trans-$[Ni(bpmp)(H_2O)_2]^{2+}$ cations, chloride anions, and uncoordinated water molecules. A view of the complex cation is depicted in Figure 2; selected bond lengths and angles in the structure are listed in Table 4.

The cation adopts a six-coordinate geometry, the coordination being provided by two *cis* phen nitrogen atoms [N(1) and N(2)] and two *cis* pyrazolyl nitrogen atoms [N(3) and N(4)] from the ligand and by two *trans* water molecules. The free bpmp ligand adopts an extended conformation in its crystal,[4] the torsion angles N(1)–C(1)–C(13)–N(5) and N(2)–C(10)–C(20)–N(4) in the free ligand around the nominally single C–C bonds linking the phen and pyrazolyl rings being 163.6 and 164.4°, respectively. In the Ni(II) complex, of course, the pyrazolyl rings are rotated around these bonds so as to bring the nitrogen atoms N(3) and N(4) into contact with the metal, the analogous torsion angles being −39.9 and −40.5° respectively. The observed geometry is roughly octahedral, but owing to the constraints of the tetradentate ligand, the bond angles around nickel do not approximate the idealized values. Thus, the N(1)–Ni(1)–N(2) angle subtended by the phen moiety is 80.8(1)° and the open N(3)–Ni(1)–N(4) angle opposite is 99.4(1)°; the two equatorial angles of 90.3(1) and 91.0(1)° subtended by the six-membered chelating moieties, N(1)–Ni–N(4) and N(2)–Ni–N(3), respectively, are approximately 90°. The *trans* N(1)–Ni–N(3) and N(2)–Ni–N(4) angles in the equatorial plane are 167.0(1) and 166.3(1)°, respectively, while the O(1w)–Ni–O(2w) angle of 179.1(1)° is approximately linear. The equatorial "plane" is distorted, the N(2) and N(4) nitrogen atoms being disposed 0.18 and 0.16 Å, respectively, above the four-atom least-squares plane through the nitrogen atoms while N(1) and N(3) are 0.18 and 0.16 Å, respectively, below the plane. The nickel ion lies in the plane. The Ni(1)–O(2w) and Ni(1)–O(1w) interatomic distances of 2.099(2) and 2.119(2) Å [average, 2.109 Å] are indicative of relatively strong bonds between the nickel ion and the water molecule. This average value is comparable to that of 2.089 Å recently reported for the octahedral complex aqua-{*o*-[(2-pyridylmethylene)amino]benzamido}-[2-(2-pyridyl)-1,2,3,4-tetrahydroquinazolin-4-one]nickel(II) dinitrate tetrahydrate.[8] In another cyclic phen- and pyridyl-based quinquedentate nickel(II) complex, where the geometry is pentagonal bipyramidal, the analogous bond lengths with two water molecules are 2.101(5) and 2.076(5) Å.[9] In the present complex the chemically nonequivalent pyrazolyl and phen nitrogen atoms are acting as chemically equivalent donors, with the Ni–N(pyz) bond lengths very slightly shorter than the Ni–N(phen) bond lengths. In a copper complex with this bpmp ligand studied earlier, the same trend was observed.[4] The dihedral angles between the pyrazolyl ring containing the N(3) and N(6) atoms to that of phen is 34.8°, that between the other pyrazolyl ring and phen is 34.6° and that between the two pyrazolyl rings is 60.2°.

There is one uncoordinated water molecule per cation in the crystals. This solvent molecule forms weak intermolecular hydrogen bonds to the chloride anions, with O(3w)···Cl(1) and O(3w)···Cl(2) separations of 3.247(3) and 3.277(3) Å, respectively, and associated H···Cl distances and O–H···Cl angles of 2.24 Å and 160° and 2.48 Å and 161°, respectively. In addition, there are strong hydrogen bonds between the coordinated water molecules and the chloride anions. Thus, coordinated water molecule O(1w) forms hydrogen bonds to Cl(1) and Cl(2), with O(1w)···Cl(1) and O(1w)···Cl(2) separations of 3.159(3) and 3.145(3) Å, respectively, and associated H···Cl distances and O–H···Cl angles of 2.44 Å and 171° and 2.36 Å and 173°, respectively. Similarly, O(2w) exhibits O(2w)···Cl(1) and O(2w)···Cl(2) separations of 3.115(3) and 3.179(3) Å, respectively, and associated H···Cl distances and O–H···Cl angles of 2.28 Å and 168° and 2.36 Å and 172°, respectively. These distances are consistent with earlier reports of O···Cl hydrogen bonding interactions.[10]

$[Ni(dpmp)Cl_2]{\cdot}CH_3CN$. The structure consists of neutral $[Ni(dpmp)Cl_2]$ molecules and uncoordinated acetonitrile solvent molecules. The neutral complex adopts a five-coordinate geometry, the coordination being provided by two phen nitrogen

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Table 5. Selected Bond Lengths (Å) and Angles (deg) in $C_{23}H_{25}Cl_2N_5NiO$

Bond Lengths			
Ni(1)–Cl(1)	2.289(3)	Ni(1)–Cl(2)	2.340(3)
Ni(1)–N(1)	2.020(9)	Ni(1)–N(2)	2.120(12)
Ni(1)–N(3)	2.078(11)		
Bond Angles			
Cl(1)–Ni(1)–Cl(2)	143.1(1)	Cl(1)–Ni(1)–N(1)	106.5(2)
Cl(2)–Ni(1)–N(1)	109.7(2)	Cl(1)–Ni(1)–N(2)	93.6(2)
Cl(2)–Ni(1)–N(2)	85.5(2)	N(1)–Ni(1)–N(2)	80.5(4)
Cl(1)–Ni(1)–N(3)	95.2(2)	Cl(2)–Ni(1)–N(3)	91.2(2)
N(1)–Ni(1)–N(3)	91.1(4)	N(2)–Ni(1)–N(3)	169.3(4)

atoms [N(1) and N(2)], the N(3) nitrogen atom from the 3,5-dimethylpyrazolyl ring and by two chloride ions. A view of the complex is depicted in Figure 3; selected bond lengths and angles in the structure are listed in Table 5.

As was noted earlier, the observed geometry is best described as a distorted trigonal bipyramid with nitrogen atoms N(2) and N(3) axial while N(1) and two chloride ligands are equatorial. In this model we expect that nickel and the three equatorial ligands should be coplanar, while the axial ligands should be disposed more or less equally above and below the plane. The mean deviation from the four-atom least-squares plane through Ni(1), N(1), Cl(1), and Cl(2) is only 0.039 Å with the three ligand atoms lying slightly on one side of the plane and Ni on the other; no atom lies more than 0.078 Å out of the least-squares plane. Because of the steric constraints of the tridentate ligand, the bond angles around the nickel, do not approximate the idealized values. Thus, the N(1)–Ni(1)–Cl(1), N(1)–Ni(1)–Cl(2), and Cl(1)–Ni(1)–Cl(2) equatorial angles of 106.5, 109.7, and 143.1°, respectively, deviate markedly from the idealized values of 120°; the axial angle N(2)–Ni(1)–N(3) is 169.3(4)° instead of 180°. As expected for a trigonal bipyramidal complex, the equatorial phenanthroline nitrogen to metal bond length Ni–N(1) of 2.020(9) Å is shorter than the corresponding axial Ni–N(2) bond length of 2.120(12) Å.

The closest distance from the central metal ion to the oxygen, O(1), of the hanging pendant is 4.721 Å, an indication of no long-range physical interaction. This complex also contains an acetonitrile molecule of solvation in its crystal, but this solvent molecule does not approach the nickel atom of the complex, the closest Ni–N (acetonitrile) separation being 5.265 Å.

Conclusion. We have succeeded in synthesizing new ligands based on 2,9-disubstituted phen and pyrazolyl moieties which can coordinate to nickel(II) in different modes and geometries than those observed for their 2,9-disubstituted phen analogues.

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Supplementary Material Available: Tables S1 and S2 (hydrogen atom parameters and anisotropic thermal parameters for the bpmp complex) and Tables S3 and S4 (hydrogen atom parameters and anisotropic thermal parameters for the dpmp complex) (6 pages). For ordering information, see any current masthead page. Listings of observed and calculated structure amplitudes for the complexes are available from D.J.H. on request.