# Bivalent Metal Complexes of N-(2-Pyridylmethyl)-2-(ethylthio)acetamide

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*Nickel(II), palladium(II), platinum(II), and copper (II) complexes of N-(2-pyridylmethyl)-2-(ethylthio)-acetamide (ptgH) have been studied. In the diamagnetic square-planar complexes $[M(ptg)X]\cdot nH_2O$ (M = Pt, Pd, Ni) the amide group is coordinated through its deprotonated N atom, ptg being N,N,S-terdentate, while in the paramagnetic six-coordinated nickel complexes $Ni(ptgH)_2X_2\cdot 2H_2O$ the amide group is coordinated through its O atom, ptgH being N,O-bidentate. In the tetragonal copper complexes $Cu(ptg)X\cdot nH_2O$ ptg acts similarly as in $[M(ptg)X]\cdot nH_2O$, the axial positions being occupied weakly by $H_2O$ molecules, whereas in the complexes $Cu(ptgH)X_2$ the amide group exists in a rarely found iminol form, ptgH being N,N,S-terdentate. Only the complex $Cu(ptg)ClO_4\cdot 1/2H_2O$ shows a subnormal magnetic moment which may be due to copper–copper interaction through an amide group.*

## Introduction

There has been no definite evidence that a free acid amide exists in an iminol form.[1] The iminol form of some acid amides may be stabilized on coordination to certain metal ions. Such an example was found in the platinum(II) complexes of pivalamide[2] and the cobalt(III) complex of glycylglycine.[3,4] The present author has found another example of the iminol form in copper(II) complexes of N-(2-pyridylmethyl)-2-(ethylthio)acetamide, $C_5H_4N–CH_2NHCOCH_2SC_2H_5$ (abbreviated as ptgH). The behaviour of ptgH is very different from that of the isomeric ligand, N-(2-ethylthioethyl)picolinamide, $C_5H_4N–CONHCH_2CH_2SC_2H_5$ (etepH)[5] which coordinates in the usual way through an amide-O or -N atom. In this study, platinum(II), palladium(II), nickel(II) and copper(II) complexes of ptgH have been prepared and coordinating properties of these two ligands are compared.

## Experimental

### Synthesis of the Ligand ptgH

A mixture of 2-picolylamine and ethyl 2-(ethylthio)-acetate in a 1:1 molar ratio was refluxed for six hrs.

and then distilled under reduced pressure (200–202° C/10 mmHg). The yield was 60%. Its picrate melts at 142.5–143.5° C.

*Analysis.* Found: C, 43.78; H, 4.01; N, 15.94%. Calcd. for the picrate $C_{16}H_{17}O_8N_5S$: C, 43.78; H, 3.90; N, 15.98%.

### Syntheses of the Complexes

Colours and analytical data are given in Table I.

$M(ptg)X\cdot nH_2O$ (M = Pt, Pd, Cu; X = Cl, Br, NCS, $ClO_4$): to an aqueous solution of a metal salt was added an ethanolic solution of ptgH in a 1:1 molar ratio and the mixture was concentrated to a small volume. The products were recrystallized from chloroform (Pt, Pd) or from water (Cu).

$Ni(ptgH)_2X_2\cdot mH_2O$ (X = Cl, Br, NCS) and Cu$(ptgH)X_2$ (X = Cl, Br, $NO_3$): these complexes were prepared by mixing an ethanolic solution of ptgH and of a metal salt in a 1:1 molar ratio at room temperature.

$Ni(ptg)(NCS)\cdot 1/2H_2O$: to an aqueous solution of nickel thiocyanate was added an ethanolic solution of a stoichiometric amount of ptgH and then an equivalent amount of sodium hydroxide dissolved in a small amount of water. The product was recrystallized from a mixture of water, ethanol, and chloroform.

### Measurements

All the measurements were carried out in the way reported previously.[5]

## Results and Discussion

### Characterization of the Ligand, ptgH

The PMR spectrum of ptgH, $CH_3CH_2(\alpha)SCH_2(\beta)$$CONHCH_2(\gamma)-C_5H_4N$, in $CDCl_3$ showed the following signals (assignments[6] in parentheses): a double quartet at $\delta = 8.49$ ppm (pyridine ring 6-H), a broad singlet at 8.05(amide-H), a complex multiplet around 7.5(3-, 4-, and 5-H atoms of pyridine ring), a doublet at 4.57($\gamma$-CH$_2$), a singlet at 3.29($\beta$-CH$_2$), a quartet at 2.61($\alpha$-CH$_2$), and a triplet at 1.24(CH$_3$). The doublet due to $\gamma$-CH$_2$ (J = 5.5 Hz) is caused by coupling with the amide-H.[6] The IR spectrum showed the charac-

TABLE I. Colours and Analytical Data for the Complexes

| | Complex | Colour (Calcd.) | M % (Calcd.) | N % (Calcd.) | Other % (Calcd.) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Pt(ptg)Cl | Light yellow | | 6.36 (6.37) | C: | 26.58 (27.31) | H: | 2.48 (2.98) | |
| 2 | Pd(ptg)Cl | Yellow | 30.01 (30.30) | 7.92 (7.98) | Cl: | 10.00 (10.10) | | | |
| 3 | Pd(ptg)Br | Yellow | 26.75 (26.90) | 7.16 (7.08) | C: | 30.21 (30.36) | H: | 3.41 (3.31) | |
| 4 | Pd(ptg)(NCS) | Yellow | 28.20 (28.47) | 11.35 (11.24) | | | | | |
| 5 | Ni(ptg)(NCS)·1/2H$_2$O | Reddish brown | 18.19 (18.06) | 12.61 (12.92) | C: | 40.56 (40.64) | H: | 4.11 (4.34) | |
| 6 | Ni(ptgI1)$_2$Cl$_2$·2H$_2$O | Light blue | 10.23 (10.01) | 9.38 (9.56) | Cl: | 12.17 (12.10) | | | |
| 7 | Ni(ptgH)$_2$Br$_2$·2H$_2$O | Light blue | 8.87 (8.70) | 8.10 (8.30) | Br: | 23.86 (23.76) | | | |
| 8 | Ni(ptgH)$_2$(NCS)$_2$ | Blue | 9.99 (9.89) | 14.07 (14.16) | | | | | |
| 9 | Cu(ptg)Cl·2H$_2$O | Blue | 18.69 (18.46) | 8.09 (8.14) | H$_2$O: | 10.71 (10.46) | | | |
| 10 | Cu(ptg)Br·2H$_2$O | Blue | 16.39 (16.35) | 7.02 (7.21) | H$_2$O | 9.44 (9.27) | | | |
| 11 | Cu(ptg)ClO$_4$·1/2H$_2$O | Dark green | 16.62 (16.67) | 7.37 (7.35) | H$_2$O: | 2.47 (2.36) | | | |
| 12 | Cu(ptgH)Cl$_2$ | Blue | 18.60 (18.43) | 8.10 (8.13) | Cl: | 20.66 (20.57) | | | |
| 13 | Cu(ptgH)Br$_2$ | Bluish green | 14.80 (14.65) | 6.52 (6.46) | Br: | 36.93 (36.85) | | | |
| 14 | Cu(ptgH)(NO$_3$)$_2$ | Blue | 16.00 (15.97) | 14.56 (14.08) | C: | 30.26 (30.10) | H: | 3.48 (3.55) | |

teristic bands of a secondary acid amide (Table II and Figure 1).[7]

## Characterization of the Complexes

### PMR spectra

In the PMR spectrum of diamagnetic [Ni(ptg)(NCS)]·1/2H$_2$O in CDCl$_3$, the signal due to the amide-H disappeared and the doublet due to $\gamma$-CH$_2$ turned to a singlet at 4.48 ppm. Thus deprotonation of the amide group is indicated. The solubilities of the diamagnetic palladium and platinum complexes are too low to record PMR spectra.

### IR spectra

From the IR spectral patterns (Table II and Figure 1) the complexes (Table I) are divided into the three classes; A: Ni(ptgH)$_2$X$_2$·mH$_2$O (X = Cl, Br, NCS); B: [Pt(ptg)Cl], [Pd(ptg)X] (X = Cl, Br, NCS), and Cu(ptg)X·nH$_2$O (X = Cl, Br, ClO$_4$); and C: Cu(ptgH)X$_2$ (X = Cl, Br, NO$_3$). On the basis of our previous works[5,8–11], it is shown that in the class A complexes the amide group is coordinated through its O atom (Formula I), and in the class B through its deprotonated N atom (Formula II). The features of the amide bands of the class C complexes are very
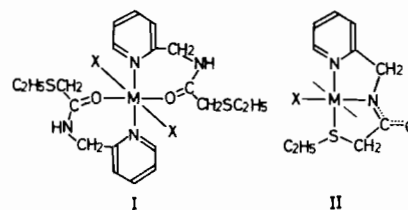


different from those of either the class A or the B complexes, so that the class C complexes seem to be a new type.

The directions of shifts of the amide I and II bands observed when going from the class B to the class C complexes (Table II) are closely related with the directions of shifts[12] of $\nu_{as}$(C=O) and $\nu_s$(C=O), respectively, of a carboxylate ion (–C$\begin{smallmatrix}O^-\\O\end{smallmatrix}$) caused by its protonation to form a carboxylic acid group (–C$\begin{smallmatrix}O\\OH\end{smallmatrix}$).

Thus the amide-O atom of the class C complexes is proposed to be protonated.

The delocalized C⋯O and C⋯N bonds of an N-coordinated amide group (Formula II) become localized

TABLE II. Selected Infrared Spectral Bands of the Ligand and Complexes ($cm^{-1}$).

| | Compound | $\nu$N–H | Amide band | | | Pyridine band | |
|---|---|---|---|---|---|---|---|
| | | | I | II | III | A | B |
| | ptgH | 3285 | 1653 | 1525 | 1252 | 1591 | 1568 |
| | **Class A complex** | | | | | | |
| 6 | $Ni(ptgH)_2Cl_2 \cdot 2H_2O$ | 3155 | 1616 | 1547 | 1315 | (1605)[a] | 1567 |
| 6' | $Ni(ptgD)_2Cl_2 \cdot 2D_2O$[b] | 2315 | 1615 | 1486 | 959 | c | 1568 |
| | **Class B complex** | | | | | | |
| 1 | Pt(ptg)Cl | | 1602 | 1389 | | (1608) | 1559 |
| 2 | Pd(ptg)Cl | | 1598 | 1386 | | 1603 | (1560) |
| 9 | $Cu(ptg)Cl \cdot 2H_2O$ | | 1596 | 1382 | | (1608) | 1559 |
| 11 | $Cu(ptg)ClO_4 \cdot 1/2H_2O$ | | 1588 | 1409 | | 1610 | 1557 |
| | **Class C complex** | $\nu$O–H | | | | | |
| 12 | $Cu(ptgH)Cl_2$ | $\begin{cases} 2645 \\ 2450 \\ 2285 \end{cases}$ | (1641) 1675 | 1368 1378 | 1308 | 1607 | 1567 |
| 12' | $Cu(ptgD)Cl_2$[b] | $\begin{cases} 1986 \\ 1926 \\ 1855 \end{cases}$ | 1660 | 1367 1376 | 1228 | 1606 | 1569 |
| 13 | $Cu(ptgH)Br_2$ | $\begin{cases} 2700 \\ 2520 \\ 2380 \end{cases}$ | 1671 | 1360 1372 | 1275 | 1605 | 1564 |
| 13' | $Cu(ptgD)Br_2$[b] | $\begin{cases} 2080 \\ 1925 \\ 1840 \end{cases}$ | 1663 | 1364 1375 | 1223 | 1606 | 1565 |
| 14 | $Cu(ptgH)(NO_3)_2$ | $\begin{cases} 2500 \\ 2270 \end{cases}$ | 1664 | 1363 1375 | 1233 | 1609 | 1564 |

[a] Figures in parentheses are referred to shoulders. [b] Deuterated complex. [c] Obscured by the amide I band at 1615 $cm^{-1}$.
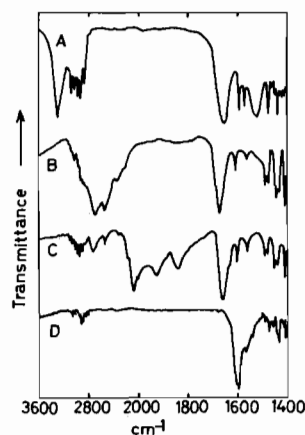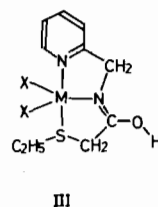


Figure 1. Infrared spectra of the ligand and complexes. A: ptgH, B: $Cu(ptgH)Br_2$ (class C), C: $Cu(ptgD)Br_2$ (class C, deuterated), and D: dehydrated $Cu(ptg)Cl$ (class B).



III

upon protonation of its O atom (Formula III) forming C=N and C–O bonds.[13, 14] Therefore, the band in the region 1664–1675 $cm^{-1}$ is assigned to $\nu$(C=N) and that in the region 1360–1378 to $\nu$(C–O). The band

$\nu$(C=N) was found at 1700 $cm^{-1}$ for the amide group in an iminol form of $[Co(glyglyH)_2]ClO_4$, where glyglyH is a glycyl-glycine anion.[3, 4] This supports the assignment of $\nu$(C=N) and the presence of the amide group in an iminol form in the class C complexes.

Unusual bands observed between 2200–2800 $cm^{-1}$ (Figure 1) for the class C complexes, which shifted markedly on deuteration as well as on exchange of anions (Table II), seem to arise from an O–H hydrogen-bonded to the anions. The band indicated as the amide III in Table II is assigned tentatively to a deformation mode of a C–O–H$\cdots$X group, since the band shifted also on deuteration and on replacement of anions. Other far IR bands arising from the amide group are given in Table III.

TABLE III. Selected Far Infrared Spectral Bands of the Ligand and Complexes $(cm^{-1})$.

| | Compound | Pyridine band | | νC–S | πN–H | δC=O | πC=O | νN–Mᵃ | νM–Xᵇ | νM–S |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | D | | | | | | | |
| | ptgH | 622 | 403 | 697 | 610 | | 490 | | | |
| | **Class A complex** | | | | | | | | | |
| 6 | Ni(ptgH)₂Cl₂·2H₂O | 645 | 433 | 704 | 652 | 581 | 511 | | | |
| 6' | Ni(ptgD)₂Cl₂·2D₂Oᶜ | 645 | 433 | 705 | 466 | 540 | 508 | | | |
| | **Class B complex** | | | | | | | | | |
| 1 | Pt(ptg)Cl | 662 | 430 | 681 | | 574 | 475 | 348 | 323 | 343 |
| 2 | Pd(ptg)Cl | 655 | 423 | 675 | | 574 | 472 | 361 | 309 | 335 |
| 9 | Cu(ptg)Cl·2H₂O | 648 | 420 | 672 | | 576 | 474 | 359 | 267 | 318 |
| 11 | Cu(ptg)ClO₄·1/2H₂O | 655 | 421 | ᵈ | | 577 | 495shᵉ 485 472sh | 337 | | 308 |
| | **Class C complex** | | | | πO–H | | | | | |
| 12 | Cu(ptgH)Cl₂ | 647 | 428 | 672sh | 847 | 570 | 458 | 346 | 309,253 | ᵈ |
| 12' | Cu(ptgD)Cl₂ᶜ | 647 | 429 | 672sh | 616 | 566 | 449 | 341 | 308,253 | ᵈ |
| 13 | Cu(ptgH)Br₂ | 646 | 525 | 673sh | 773 | 566 | 455 | 335 | 284,248 | 303 |
| 13' | Cu(ptgD)Br₂ᶜ | 646 | 426 | 674sh | 585 | 546 | 445 | 330 | 284,249 | 303 |
| 14 | Cu(ptgH)(NO₃)₂ | 648 | 423 | 671 | 776 | 572 | 464 | 355 | 304,259 | ᵈ |

ᵃ Metal–amide-N stretching vibration. ᵇ Metal–anion stretching vibration. ᶜ Deuterated complex. ᵈ Not assigned.
ᵉ sh = shoulder.

The bands due to the pyridine ring of free ptgH at 1591, 955, 622, and 403 $cm^{-1}$ were observed at higher frequencies for all the complexes (Tables II and III) implying coordination of the ring.[15,16] The weak band at 697 $cm^{-1}$ of free ptgH assigned tentatively to $\nu$(C–S) showed low frequency shift by *ca.* 15–25 $cm^{-1}$ for the class B and C complexes, whereas it did not for the class A complexes. Thus for the former two classes coordination of the S atom of ptgH is suggested, while it may be free from coordination in the class A complexes.[17]

The IR spectral bands assignable to NCS of Ni (ptgH)₂(NCS)₂ at 2095, 793, 468, and 481 $cm^{-1}$ suggest its N-coordination.[18] The spectral features of [Pd(ptg)NCS)] and [Ni(ptg)(NCS)]·1/2H₂O resemble greatly each other to suggest a similar structure with an N-bonded NCS group (Formula II, X = NCS), since their NCS bands were observed at 2122, 787, 454(Pd), and 2111, 784, 460(Ni) $cm^{-1}$. A broad strong band at 1096 and a medium one at 622 $cm^{-1}$ are observed for Cu(ptg)ClO₄·1/2H₂O suggesting non-coordination of ClO₄.[19]

*Electronic Spectra*

*(i) Diamagnetic Pt, Pd, and Ni complexes.* The spectra of these complexes are typical of square-planar $d^8$ complexes (Table IV).[20] The spectrum of [Ni (ptg)(NCS)]·1/2H₂O is similar to those of the corresponding [NiL(NCS)] (L = deprotonated terdentate

picolinamide derivative).[5,10] The spectra of the platinum and palladium complexes of ptgH are, however, different even from the spectra of those of etepH.[9] Both ptgH and etepH have apparently the same donor atoms: pyridine-N, thioether-S, amide-N and halogen atom X (Formula II). However, the property of an amide-N atom seems to be different, because the amide group of ptgH is aliphatic, while that of etepH is aromatic. This may be reflected on the electronic properties of the complexes.

*(ii) Paramagnetic Ni complexes.* The diffuse reflectance spectrum (Table V) of Ni(ptgH)₂(NCS)₂ is different from that of Ni(C₂H₅SCH₂CONH₂)₂(NCS)₂ with an octahedral 2N2O2S chromophore.[21] In view of this and the results of the IR spectrum, a *trans*-4N2O structure (Formula I, X = NCS) is proposed for Ni(ptgH)₂(NCS)₂. Based on the approximately $D_{4h}$ structure, the spectrum can be assigned and the following parameters calculated[22] seem to be reasonable: Dq(xy) = 1070 and Dq(z) = 590 $cm^{-1}$ where Dq(xy) is the average ligand field strength of the pyridine-N' and NCS-N in an xy plane and Dq(z) is that of the amide-O atoms along a z axis.

The spectra of Ni(ptgH)₂X₂·2H₂O (X = Cl, Br) (Table V), which are characteristic of a six-coordinate Ni(II) complex,[23] are identical to each other and independent of halide ions. This is consistent with the absence of $\nu$(Ni–X). Although the two complexes

TABLE IV. Absorption Spectra of the Complexes in Chloroform ($\times 10^3$ cm$^{-1}$).

| | Complex of ptgH | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ |
|---|---|---|---|---|---|---|
| 1 | Pt(ptg)Cl | 23.7sh[a] | 27.9sh | 30.7(3.13)[b] | 36.5(3.77) | |
| 2 | Pd(ptg)Cl | 19.5sh | 23.5sh | 29.0(3.17) | 34.1sh | |
| 3 | Pd(ptg)Br | 19.3sh | 22.7sh | 28.0(3.10) | 33.5sh | |
| 4 | Pd(ptg)(NCS) | | 23.7sh | 29.4sh(3.2) | 34.3sh | |
| 5 | Ni(ptg)(NCS)·1/2H$_2$O | 14.5sh | 18.0sh | 21.3(2.74) | 30.8sh | |
| 9 | Cu(ptg)Cl·2H$_2$O | | 16.3(2.51) | 20.0sh | 29.3sh | |
| 10 | Cu(ptg)Br·2H$_2$O | | 16.2(2.46) | 19.7sh | 28.7sh | |
| | **Complex of etepH for reference** | | | | | |
| | Pt(etep)Cl·H$_2$O | 19.5sh | 25.1(3.24) | 28.2sh | 30.6sh | 33.8sh |
| | Pd(etep)Cl·2/3H$_2$O | | 23.9sh | 28.3sh | 29.7(3.53) | 37.3sh |
| | Cu(ctcp)Cl·H$_2$O | | 16.3(2.47) | 19.5sh | | 31.0(3.78) |

[a] sh = shoulder. [b] Figures in parentheses are log$\varepsilon$, where $\varepsilon$ is a molar extinction coefficient.

TABLE V. Magnetic Moments and Diffuse Reflectance Spectra.

| | Complex of ptgH | $\mu_{eff}$ B.M. | Absorption Maximum ($\times 10^3$ cm$^{-1}$) |
|---|---|---|---|
| 5 | Ni(ptg)(NCS)·1/2H$_2$O | Dia.[a] | 14.5sh[b] 17.6sh |
| 6 | Ni(ptgH)$_2$Cl$_2$·2H$_2$O | 3.24 | 8.9, 13.9sh, 15.2, 25.6 |
| 7 | Ni(ptgH)$_2$Br$_2$·2H$_2$O | 3.28 | 8.9, 13.9sh, 15.2, 25.6 |
| 8 | Ni(ptgH)$_2$(NCS)$_2$ | 3.28 | 8.3, 10.7, 14.1sh, 16.0, 21.5sh, 26.3 |
| 9 | Cu(ptg)Cl·2H$_2$O | 1.81 | 16.6, 20.8sh, 26.8sh |
| 10 | Cu(ptg)Br·2H$_2$O | 1.84 | 16.7, 20.2sh, 25.5sh |
| 11 | Cu(ptg)ClO$_4$·1/2H$_2$O | 1.49 | 16.2, 23.5sh |
| 12 | Cu(ptgH)Cl$_2$ | 1.86 | 14.3, 18.0sh, 28.0sh |
| 13 | Cu(ptgH)Br$_2$ | 1.83 | 14.1, 17.5sh, 24.5sh |
| 14 | Cu(ptgH)(NO$_3$)$_2$ | 1.86 | 15.6, 18.0sh, 28.5sh |
| | **Complex of etepH for reference** | | |
| | Ni(etepH)$_2$Cl$_2$ | 3.22 | 9.2, 14.9, 17.0sh |
| | Ni(etepH)$_2$(NCS)$_2$ | 3.18 | 10.3, 13.2w, 16.5 |
| | Cu(ctcp)Cl·H$_2$O | 1.83 | 15.3, 18.5sh, 26.0sh |
| | Cu(etepH)Cl$_2$ | 1.88 | 13.1, 25.0sh |

[a] Dia. = diamagnetic. [b] sh = shoulder, w = weak.

have formally a *trans*-4O2N chromophore (Formula I, X = H$_2$O), the band of the transition $^3T_{2g} \leftarrow {}^3A_{2g}$ was only broadened without splitting. As was shown above, the ligand field of the amide-O atom of ptgH is very weak and then the symmetry around the Ni atom may be much lower than D$_{4h}$. In such a case the three splitting components of $^3T_{2g} \leftarrow {}^3A_{2g}$ are known usually to give a broad band.[23]

*(iv) Cu complexes.* The magnetically subnormal complex Cu(ptg)ClO$_4$·1/2H$_2$O exhibited a pronounced shoulder at $23.5 \times 10^3$ cm$^{-1}$. The origin of the shoulder may be the same as that of the bands in this region observed for other magnetically subnormal Cu(II) complexes.[24,25] Subnormal magnetic moments

of Cu(II) complexes arise usually from interaction of electron spins through appropriate orbitals between copper ions.[26,27] In this case, a most probable pathway may be p-$\pi$ orbitals delocalized over an amide group (Formula II) which can be overlapped with either a $d_{xz}$ or $d_{yz}$ orbital of copper ions, for the O atom of an N-coordinated amide group has still an ability of coordination,[11] so that the group can act as a bridge between two copper ions. A similar assumption has been made for magnetically subnormal Cu(II) complexes of oxamide derivatives.[28,29]

Cu(ptg)X·2H$_2$O (X = Cl, Br) showed a characteristic spectrum of a tetragonal Cu(II) complex and may have the structure shown in Formula II, the apical sites of which are weakly occupied by H$_2$O molecules. The

spectra of the class C $Cu(ptgH)X_2$ (X = Cl, Br, $NO_3$) depend on anions (Table V), indicating their coordination (Formula III). Appearance of $\nu(Cu–X)$ is consistent with this (Table III). Coordination of $NO_3$ is clearly shown[30] for $Cu(ptgH)(NO_3)_2$ by the presence of three strong bands at 1483, 1273, 'and 1002, and a medium one at 807 cm$^{-1}$. These electronic spectra showed red-shift compared with those of the class B $Cu(ptg)X \cdot 2H_2O$ (X = Cl, Br), implying a smaller tetragonal distortion or a trigonal bipyramidal arrangement in the class C complexes.[31]

The possibility of amide-O coordination of ptgH in the class C complexes like in $Cu(etepH)Cl_2$[5] is excluded because the spectrum of $Cu(etepH)Cl_2$ is markedly different from that of $Cu(ptgH)Cl_2$. The chemical compositions of the two are the same, but the modes of coordination of the amide groups are quite different. In $Cu(ptgH)Cl_2$ ptgH is in an iminol form and coordinated through pyridine-N, amide-N, and thioether-S atoms (Formula III), while in $Cu(etepH)Cl_2$ etepH is coordinated with pyridine-N and amide-O atoms.[5]

## Conclusion

It is interesting that ptgH forms diamagnetic square-planar $[Ni(ptg)(NCS)] \cdot 1/2H_2O$, whereas etepH, an isomer of ptgH, forms no nickel(II) complexes of this type.[5] However, paramagnetic $Ni(LH)_2X_2 \cdot mH_2O$ were obtained for both ptgH and etepH. For both ligands, palladium(II) and platinum(II) gave only the complex $[MLX] \cdot nH_2O$, while copper(II) gave two types: $[CuLX] \cdot nH_2O$ and $Cu(LH)X_2$. Although the apparent formulae are the same for ptgH and etepH, the properties of $Cu(LH)X_2$ are very different between the two ligand as was discussed above.

The iminol form coordination of an amide group seems to be an intermediate for deprotonated N-coordination,[4, 13, 14] and it is shown that the amide group of ptgH is more liable to be deprotonated than that of the isomeric etepH. The liability is also true for nickel(II), namely, ptgH gives $[Ni(ptg)(NCS)] \cdot 1/2H_2O$, whereas etepH gives no complex of this type.

The condition for coordination of an amide group in an iminol form appears to be very delicate and limited, since for the picolinamide derivatives so far studied, only the complexes coordinated with amide-O or deprotonated amide-N atoms have been obtained. Factors such as the coordinating ability of substituents on an amide group, properties of central metal ions, and preparative conditions may affect the coordinating mode of an acid amide group and only when certain conditions are satisfied, coordination of an acid amide in an iminol form may be allowed.

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