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# Polymer Complexes: supramolecular assemblies and structures of poly[*N*-(2′-pyridyl)propenamide] complexes

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**A number of new polymer complexes of palladium(II), platinum(II) and copper(II) containing homopolymer (*N*-(2′-pyridyl)propenamide; APH) and various anions ($Cl^-$, $Br^-$, $I^-$ or $NO_3{}^-$) have been synthesized and characterized by elemental analyses, magnetic susceptibility, electron paramagnetic resonance, IR and reflectance spectral measurements. The homopolymer shows three types of coordination behavior. In the mononuclear polymer complexes 1–6 and 9 it acts as a neutral bidentate ligand chelated through the pyridine-nitrogen and amide-oxygen atoms, whereas in the square-planar $[Pd(APH)_2X_2]$ (X = Cl, Br) unidentate APH is coordinated through the pyridine-nitrogen atom alone. Under alkaline conditions APH is deprotonated in the presence of palladium(II) to form $[Pd(AP)_2]$ (10), AP being an anionic bidentate ligand and chelating through the pyridine-nitrogen and amide-oxygen atoms. The poly-chelates are of 1 : 1 and 1 : 3 (metal : homopolymer) stoichiometry and exhibit six-coordination. The polymer complexes of stoichiometric $[(APH)_2CuX_2]$ contain square planar $(APH)_2$ $Cu^{2+}$ units and the anions $X^-$ are in the axial positions, giving distorted octahedral configurations. From the electron paramagnetic resonance and spectral data, the orbital reduction factors were calculated. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** supramolecular structures; solid complexes; EPR; ligand field parameters

## INTRODUCTION

Homopolymers have played a key role in our understanding of the coordination chemistry of transition-metal ions. Transition-metal complexes of bidentate homopolymer ligands are always of interest[1–6] since they exhibit a marked tendency to oligomerize, thus leading to novel structural types, and they display a wide variety of magnetic properties.

The coordination chemistry of platinum complexes of heterocyclic compounds containing nitrogen has received considerable attention. El-Sonbati and co-workers[1–5] studied the ligating behaviour of poly-heterocyclic compounds containing nitrogen with the first-row transition elements and assigned planer, tetrahedral or octahedral geometry to the complexes based on the magnetic data.

An acid amide group has two donor atoms, nitrogen and oxygen, and it depends upon the experimental conditions as to which one of them coordinates to the metal ions.

Poly(*N*-(2′-pyridyl)propenamide) (poly(APH)) is capable of chelation by means of the heterocyclic nitrogen atom and a donor oxygen atom of the side chain. It was decided, therefore, to isolate a variety of palladium(II), platinum(II) and copper(II) complexes of poly(APH) with common anions. In particular, we investigate the possible halogeno and nitrato bonding through IR spectral studies of copper(II) complexes with common halogen ions. We have demonstrated the correlations between metal–nitrogen, metal–oxygen and metal–anions (X = Cl, Br, I and $NO_3$) stretching frequencies.

Recently, the design and preparation of supramolecular materials based on coordination metal ions has made considerable progress. Well-known examples of supramolecular assemblies are those constructed with

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square planar palladium(II) and platinum(II) or octahedral ruthenium(III) and rhodium(III).[3,5]

However, practically little work has been done in this field. In this paper, the results of IR, electron spectroscopic studies and magnetic measurement are presented and discussed. Also, the effect of the ligand field parameters of electron paramagnetic resonance (EPR) were studied.

## EXPERIMENTAL

The experimental technique has been described previously.[1–5]

### Reagents

2-Aminopyridine was bought from Aldrich and used without further purification. Acryloylchloride (Aldrich) was used without purification. 2,2′-Azobisisobutyronitrile (AIBN) was purified by fraction crystallization from EtOH.[7]

APH monomer was prepared according to literature methods.[1–5] The IR spectrum of the monomer showed the presence of an NH absorption band at 3350 cm$^{-1}$. Anal. Found: C, 65.0; H, 5.4; N, 19.1. Calc. for APH: C, 64.9; H, 5.4; H, 5.4; N, 18.9%. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ (ppm) 10.22 (CONH); 5.83, 5.53 ($CH_2{=}C$), 8.56 (H–Py). $^{13}$C NMR (300 MHz, DMSO-$d_6$): $\delta$ 118(1), 142(2); (3) $\delta$ 145; (4) $\delta$ 158; (5) $\delta$ 137; (6) $\delta$ 108; (7) $\delta$ 150; (8) $\delta$ 172.

### Polymerization

Monomer APH was homopolymerized by the method described by El-Sonbati and co-workers.[1–5] The homopolymer has been characterized by IR, $^1$H and $^{13}$C NMR.

### Preparation of the polymer complexes

#### *Method A: copper(II) salts, polymer complexes **1–4***

In a typical preparation, a solution of homopolymer (0.01 mol) in dimethylformamide (DMF; 20 ml), the metal salts (0.01 mol) in DMF (25 ml), and 0.1 w/v AIBN as an initiator were used. The resulting mixture was heated at reflux for 8 h. The hot solution was precipitated by addition to a large excess of distilled water containing dilute HCl to remove the metal salts that were incorporated into the polymer complexes. The polymer complexes (**1–4**, see Table 1) were filtered, washed with water, and dried in a vacuum oven at 40 °C for several days to yield 65–75% of coloured crystals.

#### *Method B: palladium(II) salts, polymer complexes **5–8***

A solution of $PdX_2$ (X = Cl or Br; 0.01 mol), APH (0.01 or 0.02 mol) and 0.1 w/v AIBN as initiator in MeOH–DMF (3 : 2, v/v) containing a few drops of concentrated HCl were mixed and stirred for 3 h at room temperature. The polymer complexes precipitated immediately; they were then refluxed for ~1.5 h to complete the reaction. They were then poured into a large excess of distilled water containing dilute HCl, to remove the metal salt incorporated into the polymer complexes. The products were filtered off, washed with water, MeOH, and $Et_2O$.

#### *Method C: platinum chloride polymer complex **9***

The salt $K_2[PtCl_4]$ was dissolved in water/EtOH (1 : 1, v/v) and APH in 0.1 M HCl; the pH of both solutions was acidic. The two solutions were mixed and stirred at room temperature for 20 h in the presence of 0.1 w/v AIBN as initiator. The obtained precipitate was filtered off and washed with small portions of water, EtOH, and $Et_2O$.

#### *Method D: Palladium polymer complex **10***

To a suspension of $Pd(APH)_2X_2$ (**6** and **7**) 50 ml of DMF/EtOH (1 : 1, v/v) was added an aqueous solution (25 ml) of KOH (0.4 g). The mixture became clear, and yellow crystals precipitated. The product was washed with water.

#### *Method E: palladium polymer complexes **11** and **12***

An ethanolic solution (0.01 mol) of $PdX_2$ (X = Cl or Br) was mixed with the appropriate weight of the corresponding monomer in EtOH (20–30 ml) and 0.1 w/v AIBN as an initiator. The reaction mixture was boiled with stirring until the corresponding solid complex separated. On cooling, the crystalline product that formed was filtered off and washed several times with EtOH.

### Measurements

Carbon, hydrogen and nitrogen microanalyses were carried out at the Cairo University Analytical Center, Egypt. The metal content in the polymer complexes was estimated by standard methods.[3–5] The $^1$H NMR spectrum was obtained with a Jeol FX90 Fourier transform spectrometer with DMSO-$d_6$ as the solvent and tetramethylsilane as an internal reference. IR spectra were recorded using a Perkin–Elmer 1340 spectrophotometer. UV–Vis spectra of the polymer were recorded in nuzol solution using a Unicam SP 8800 spectrophotometer. The magnetic moments of the solid complexes prepared were determined at room temperature using the Gouy method. Mercury(II) (tetrathiocyanato)cobalt(II), $[Hg\{Co(SCN)_4\}]$ was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood[8] and Pascal's constants. Magnetic moments were calculated using

$$\mu_{\text{eff}} = 2.84[T\chi_{\text{M}}^{\text{coor}}]^{1/2}$$

EPR measurements of powdered samples were recorded at room temperature (Tanta University, Egypt) using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenylpicrylhydrazyle (DPPH) as a reference material. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a KOH–$H_2O_2$ mixture. The halide content was then determined by titration with a standard $Hg(NO_3)_2$ solution using diphenylcarbazone as an indicator.

**Table 1.** Analytical data and methods of preparation for the polymer complexes **1**–**12** (for molecular structures see Fig. 2)

| Complex[a] | Method of preparation[b] | Experimental (calc.) (%) C | H | N | $\chi$[c] | Molar ratio (M : L) |
|---|---|---|---|---|---|---|
| $[Cu(APH)_2Cl_2]$ (**1**) | A | 44.5<br>(44.6) | 3.6<br>(3.7) | 13.3<br>(13.0) | 16.6<br>(16.5) | 1 : 2 |
| $[Cu(APH)_2Br_2]$ (**2**) | A | 36.9<br>(37.0) | 3.0<br>(3.1) | 10.9<br>(10.8) | 30.7<br>(30.8) | 1 : 2 |
| $[Cu(APH)_2I_2]$ (**3**) | A | 31.3<br>(31.2) | 2.6<br>(2.6) | 9.3<br>(9.1) | 41.5<br>(41.6) | 1 : 2 |
| $[Cu(APH)_2((NO)_3)_2]$ (**4**) | A | 39.7<br>(39.7) | 3.3<br>(3.3) | 17.6<br>(17.4) | — | 1 : 2 |
| $[Pd(APH)Cl_2]$ (**5**) | B | 29.4<br>(29.5) | 2.4<br>(2.5) | 8.8<br>(8.6) | 22.0<br>21.8 | 1 : 1 |
| $[Pd(APH)Br_2]$ (**6**) | B | 23.1<br>(23.2) | 2.0<br>(1.9) | 7.0<br>(6.8) | 38.8<br>(38.6) | 1 : 1 |
| $[Pd(APH)_2Cl_2]$ (**7**) | B | 40.5<br>(40.6) | 3.3<br>(3.4) | 12.0<br>(11.8) | 15.3<br>(15.0) | 1 : 2 |
| $[Pd(APH)_2Br_2]$ (**8**) | B | 34.0<br>(34.1) | 3.0<br>(2.9) | 10.3<br>(10.0) | 28.7<br>(28.5) | 1 : 2 |
| $[Pt(APH)Cl_2]$ (**9**) | C | 23.0<br>(23.2) | 2.0<br>(1.9) | 7.0<br>(6.8) | 17.5<br>17.2 | 1 : 2 |
| $[Pd(AP)_2]$ (**10**) | D | 48.0<br>(47.9) | 4.1<br>(4.0) | 14.3<br>(14.0) | — | 1 : 2 |
| $[Pd(AP)Cl_2]$ (**11**) | E | 33.0<br>(33.2) | 2.5<br>(2.4) | 10.0<br>(9.7) | 12.0<br>(12.3) | 1 : 1 |
| $[Pd(AP)Br_2]$ (**12**) | E | 28.9<br>(28.8) | 2.0<br>(2.1) | 8.1<br>(8.4) | 23.8<br>(24.0) | 1 : 1 |

[a] The abbreviation AP represents the deprotonated form of the monomer APH; air-stable; non-hygroscopic; insoluble in water; partially soluble in coordinating solvents such as DMF and DMSO.

[b] See text.

[c] Estimated gravimetrically, $\chi$ = Cl or Br.

## RESULTS AND DISCUSSION

### Characterization of the homopolymer

APH was prepared by the amidation reaction of acryloylchloride with 2-aminopyridine.[1–3] The monomer APH was characterized as in the Experimental section. The monomer was then polymerized by radical polymerization initiated by AIBN. The homopolymer has been characterized by various techniques.[1–5]

### IR and NMR spectra of the uncomplexed and complexed polymers

In the present work we mainly investigate the synthesis and metal chelate of the monomer (APH), as well as the influence of the different positions of the carbonyl and azomethine groups of the side residue of the monomer on their stereochemistry and chain flexibility. For this purpose, the $^{13}$C NMR spectra of both the monomer and homopolymer have been analysed comparatively (Fig. 1). The $^1$H NMR spectrum of the monomer did not show enough information for stereochemical studies.

The NMR spectrum of the monomer showed the expected peaks and pattern of the vinylic group ($CH_2{=}CH$), i.e. $\delta$ (DMSO-$d_6$) 6.57 ppm (dd, $J = 17$, 11 Hz) for the vinyl CH proton and $\delta$ 5.32 ppm (AM part of AMX system dd, $J = 17$, 1 Hz and dd, $J = 11$, 1 Hz) for the vinyl $CH_2$ proton. These peaks disappeared on polymerization, and were replaced by a triple at $\delta$ 2.2 ppm (t, $J = 7$ Hz) and a doublet at $\delta$ 1.9 ppm (d, $J = 7$ Hz). This indicates that the polymerization of the monomer occurs on the vinyl group. It is worth noting that the rest of the proton spectrum of the monomer and polymer remains almost the same.

Free APH in DMSO-$d_6$ shows three multiplets at 7.12 (pyridine ring 5-H), 7.64 (4-H) and 8.33 ppm (3,6-H), and a broad singlet at 10.41 ppm (amide N–H). Only $Pd(AP)_2$ is sufficiently soluble in DMSO-$d_6$. The spectrum shows a complex multiplet at 6.89 ppm (3,5-H), a multiplet at 7.70 ppm (4-H), and a double doublet at 8.44 ppm (6-H). The broad singlet of the free APH at 10.41 ppm (N–H) disappears on coordination, which is consistent with the disappearance of $\nu$(N–H) in the IR spectrum.

The IR spectrum of the uncomplexed polymer is a polyfunctional planar molecule with a delocalized $\pi$-electronic system, with two nitrogen atoms which may act as basic centres and a labiel N–H band. The molecule may be present in

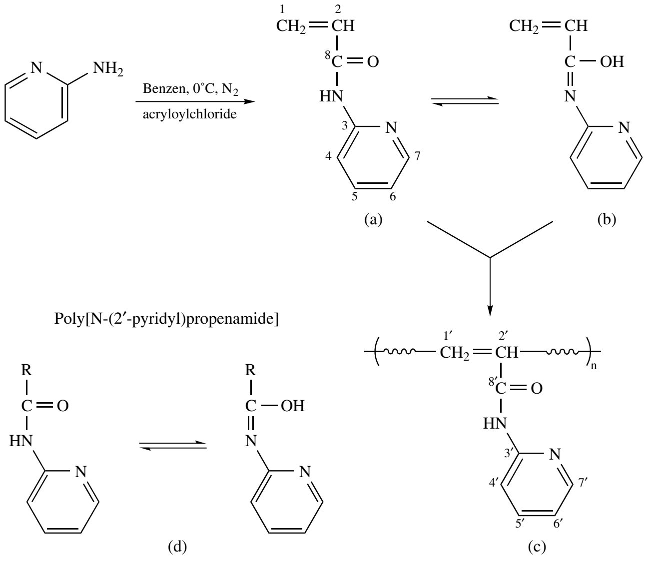


**Figure 1.** Structure of the homopolymer.

several tautomers and conformers. Its structure and dynamical behaviour have been studied in solution by $^1H$ and $^{13}C$ NMR.[1,3] The equivalent conformers in Fig. 1d are the principal contributors to the molecular structure of this molecule in solution.

The protonation and coordination of monomers were investigated using $^1H$ and $^{13}C$ NMR studies.[1] In order to obtain information about the Lewis basic sites in this molecule, substitution reactions and the blockage of the lone pair of *N*-pyridine were carried out. Information about the N–H tautomeric equilibrium of the monomer and the preferred sites for coordination (*vide supra*) was also derived. The ligand has several isomers that may be involved in coordination towards metal ions. The possible structures of the coordination compounds verify that the proposed structures are stable. Two different types of coordination compound were found. In the first, the ligand coordinates as a chelate through *N*-pyridine and CO (amide I), which is the case for most of the complexes. Compounds that contained only one ligand in the coordination sphere yield products with square-planar geometry (palladium). With two chelating APH units square-planar geometry was established for palladium and octahedral for copper. The second type of coordination behaviour was observed for palladium compounds, where the ligand was monodentate through the *N*-pyridine and the structure is square planar (Fig. 2).[9,10]

The IR spectrum of uncomplexed polymer shows absorption bands at 3350 cm$^{-1}$ and 1630 cm$^{-1}$ due to –NH and CO groups respectively. These bands disappear when the homopolymer is dissolved in DMF and four absorption bands have been observed at 1600, 1540, 1475 and 1420 cm$^{-1}$ which are attributable to $\nu_{\text{assym+sym}}$(C=C) and $\nu$(C=N) vibrations. Poly(APH) has the resonance structure shown in Fig. 1d.[9–11]

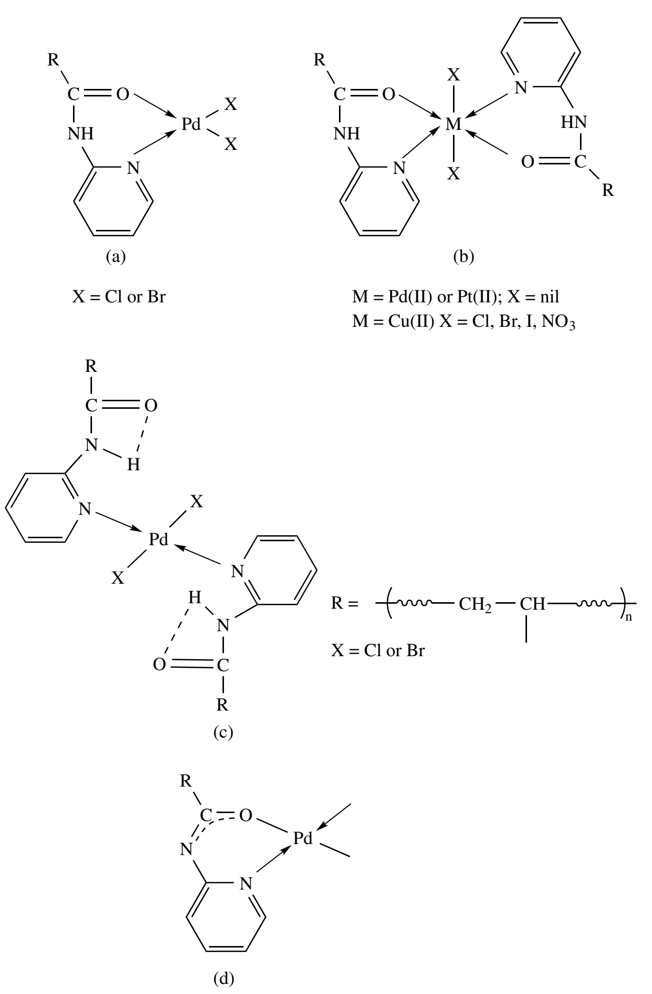


**Figure 2.** Coordination compounds of APH with transition-metal ions.

If coordination takes place with the metal ion through the nitrogen atom, then its hybridization will be sp$^3$ and the CO bond will become a double bond with loss of the resonance energy.[9,10]

The amide I ($\nu$(C=O)) band (Table 2), and the amide II ($\nu$(C=N)) and III ($\delta$(NH)) bands arise from $\nu$(C–N) as well as from $\delta$(N–H), although these modes are coupled to one another.[12] Consequently, for an amide group coordinated through the oxygen atom, the amide I band will shift to a lower frequency and the amide II and III bands will shift to higher frequencies. On the other hand, if the amide-nitrogen atom coordinates, then the amide I, II and III bands should shift in the opposite directions. The IR spectra of the copper(II) polymer complexes with homopolymer (Table 2) are, in all cases, in accordance with the oxygen atom being bonded without deprotonation of the amide nitrogen.

A comparison of the spectra of the free ligand with those of AP complexes reveals changes in pyridine ring vibrations. Band I of these vibrations shows an upward shift of 5 cm$^{-1}$. The ring breathing mode at 990 cm$^{-1}$ increases in frequency

**Table 2.** IR spectral bands due to the amide groups of the monomer and polymer complexes **1**–**12**

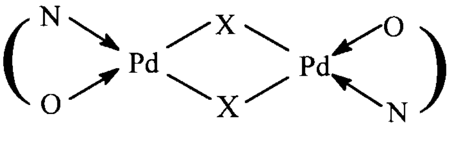
| Complex | $v$(N–H) (cm$^{-1}$) | Amide band (cm$^{-1}$) I | II | III |
|---|---|---|---|---|
| APH | 3350 | 1630 | 1530 | 1280 |
| **1** | 3320 | 1580 | 1515 | 1280 |
| **2** | 3330 | 1585 | 1500 | 1280 |
| **3** | 3335 | 1587 | 1495 | 1278 |
| **4** | 3285 | 1570 | 1490 | 1275 |
| **5** | 3325 | 1655 | 1475 | 1270 |
| **6** | 3327 | 1670 | 1472 | 1272 |
| **7** | 3340 | 1665 | 1474 | 1274 |
| **8** | 3337 | 1667 | 1470 | 1274 |
| **9** | 3342 | 1660 | 1475 | 1273 |
| **10** | —[a] | | 1430 | —[a] |
| **11** | —[a] | | 1435 | —[a] |
| **12** | —[a] | | 1432 | —[a] |

[a] These bands did not appear.

and appears at *ca.* 1005 cm$^{-1}$.[2] These changes suggest that pyridine-nitrogen coordinates to the metal atom.

The far-IR data of the polymer complexes give insight into the structure and bonding in the solid state. The $\nu$(M–Cl)$_L$ modes (M = Pd, Pt) are assigned to strong intensity bands in the region 350–340 cm$^{-1}$ for **5** and **9**; they shift to the 245–225 cm$^{-1}$ region in **6**. The appearance of these bands is consistent with the formulation [M(APH)X$_2$]. The presence of two $\nu$(M–X)$_L$ vibrations in each far-IR spectrum confirms the cis-structures of the square-planar complexes **5**, **6** and **9**.[2] In polymer complexes of stoichiometry [Pd(APH)X$_2$], the monomer coordinates to the metal ion via the heterocyclic nitrogen and the carbonyl oxygen atoms. This is further supported by the appearance of IR active bands at 285–290 ($\nu$(Pd–O)) and 470–485 cm$^{-1}$ ($\nu$(Pd–N)) vibrational modes.[2,5]

The IR spectra of [Pd(AP)X]$_2$ (X = Cl, Br) exhibit strong bands at 280 cm$^{-1}$ and 225 cm$^{-1}$, characteristic of bridging Cl and Br respectively.[13] According to the electronic and IR spectra of these complexes, the following structure could be assumed:



The spectra of the rest of the palladium(II) polymer complexes exhibit far-IR-active bands characteristic of terminal coordinated halides.[13]

Furthermore, the $\nu$(Pd–Br)/$\nu$(Pd–Cl) ratios lie in the range 0.75–0.80, supporting the assumed square-planar symmetry. An interesting point is the difference in the mode of chelation, with [Pd(APH)$_2$X$_2$] on one the side and [Pd(APH)X$_2$] on the other. The absence of a large shift of the $\nu$(CO) band indicates that there is no interaction between the CO group and the metal ion (i.e. no $\nu$(Pd–O)), whereas $\nu$(Pd–N) is exhibited at 483–475 cm$^{-1}$. Accordingly, the monomer act as if monodentate, coordinated to the palladium(II) via the heterocyclic nitrogen atom.

On the other hand, in [Pd(APH)$_2$X$_2$], there is a strong band at 350 cm$^{-1}$ and 260 cm$^{-1}$ for X = Cl and Br respectively, which is in the region[3,5] diagnostic of $\nu$(Pd–X) for *trans*-[Pd(APH)$_2$X$_2$]. Thus, these two palladium complexes seem to be square planar: the coordination is through the pyridine-nitrogen atom alone without coordination of the amide group.

The amide bands VI and IV of the deprotonated complex **10** shift to lower frequencies (Table 3) and the amide I band is observed at a very low frequency, commensurate with the mode of coordination shown in Fig. 2, in which the chelate ring is similar to that of $\beta$-diketone complexes. This structure is further supported by the disappearance of $\nu$(N–H) and the presence of a band at 290 cm$^{-1}$, which is close to the band of Pd(acac)$_2$ (acac = acetylacetone anion) observed at 295 cm$^{-1}$ ($\nu$(Pd–O)).[14]

## Geometry of the Cu$^{2+}$-polymer complexes

The electronic spectra of six-coordinate copper(II) polymer complexes (**1**–**4**) consist of a broad band with a maximum in the region 17 255–18 145 cm$^{-1}$ and with a well-defined shoulder in the range 14 685–16 758 cm$^{-1}$. Their spectral data are not consistent with those expected for five-coordinated copper(II) ions, but they are rather similar to those reported for copper(II) complexes in which the copper(II) ion is in a square-planar or octahedral environment with a very large tetragonal distortion.[15] These have been resolved by Gaussian analysis and were assigned to $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ transitions in order of increasing energy.

**Table 3.** IR spectral bands due to the amide groups of the monomer and polymer complexes **1**–**12**

| Compound | Amide band (cm$^{-1}$) IV | VI | Pyridine bands (cm$^{-1}$) |
|---|---|---|---|
| APH | 680 | 560 | 625, 416 |
| **1** | 695 | 594 | 650, 446 |
| **2** | 693 | 592 | 646, 445 |
| **3** | 694 | 593 | 645, 446 |
| **4** | 692 | 591 | 644, 444 |
| **5** | 692 | 555 | 655, 448 |
| **6** | 693 | 554 | 654, 447 |
| **7** | 695 | 556 | 653, 448 |
| **8** | 696 | 557 | 655, 449 |
| **9** | 694 | 554 | 652, 446 |
| **10** | 638 | 536 | 654, 456 |
| **11** | 645 | 525 | 635, 436 |
| **12** | 647 | 526 | 633, 430 |

The low-energy shoulder in these complexes is assigned to the $d_{x^2-y^2} \rightarrow d_{z^2}$, transition;[15] hence, the main spectral band is assigned to the $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ state and is the measure of the difference between in-plane and axial fields. Since the in-plane field is constant in all present cases, the change in the position of the bands would be due to the axial field only. In these copper(II) polymer complexes, the spectral bands are found to be sensitive to the nature of the anion X, and shift to higher energy in the order $Cl^- \leq Br^- < I^- < NO_3^-$. Thus, these spectral data suggests a tetragonally distorted octahedral geometrical shape for these complexes, where the ligand is bidentate and the axial positions are occupied by the anions (Fig. 2b). Their room-temperature magnetic moments are also consistent with those reported for copper(II) ions in tetragonally distorted environments[16] (Table 4).

## Electron paramagnetic resonance

The EPR spectra of polycrystalline powder samples of polymer complexes of copper were studied. All the complexes show EPR spectra with $g_\parallel > g_\perp$ characteristic of a tetragonally distorted octahedral geometry with the $d_{x^2-y^2}$ orbital lowest in energy. Various parameters have been calculated by the method of approximation suggested by Kneubuhl[17] and Garmen *et al.*[18] and the values are given in Table 1. The $g_\parallel$ and $g_\perp$ values obtained in these complexes are commensurate with the principal axes of the octahedra being parallel to each other and all the sites are equivalent in every orientation in the static magnetic field. In all the complexes, the $g_\parallel$ values are less than 2.3, which shows that the complexes are largely covalent. Further, the values are consistent with the Cu–N and Cu–O bonded copper complexes.

**Table 4.** The magnetic moments and the electronic spectral bands of the polymer complexes **1**–**4** (for structures see Table 1)

| Complex | $\mu_{eff}$ (B.M.)[a] | Electronic spectra (cm$^{-1}$) $\Delta_1$ | $\Delta_2$ | $\Delta_3$ |
|---|---|---|---|---|
| **1** | 1.82 | 17245 | 16140 | 14705 |
| **2** | 1.81 | 17670 | 16360 | 14715 |
| **3** | 1.80 | 17990 | 16695 | 14895 |
| **4** | 1.79 | 18120 | 16950 | 14400 |

[a] The order of $\mu_{eff}$ is C1 > Br > I > $NO_3$. Per metal. Measured at room temperature.

The stronger interaction along the $z$-axis should be accompanied by an increase in the value of $g_\parallel$. The stronger axial bonding, however, leads to an increase in the length of bond in-plane covalency and the energy of the $d_{x^2-y^2} \rightarrow d_{xy}$ transition.[19] Both these factors tend to increase the value of $g_\parallel$. The $g_\parallel$ values for the complexes studied follow the order

$$\mathrm{Cu(ligand)_2(NO_3)_2 > Cu\ (ligand)_2Cl_2}$$
$$\mathrm{> Cu(ligand)_2I_2 > Cu(ligand)_2Br_2}$$

This appears to be the order of the strength of metal–anion interactions for nitrate, chloride, bromide and iodide. Our results are in agreement with the respective positions of the anions as given in the spectrochemical series.[20] The average $g$ values ($g_{iso}$) are calculated according to

$$g_{iso} = \frac{1}{3}g_\parallel + \frac{2}{3}g_\perp \qquad (1)$$

and give values in the range 2.1103–2.1187. The EPR data are reported in Table 5. The $g_{iso}$ values for the polymer complexes studied follow the order

$$\mathrm{Cu(ligand)_2(NO_3)_2 > Cu(ligand)_2I_2}$$
$$\mathrm{> Cu(ligand)_2Cl_2 > Cu(ligand)_2Br_2}$$

In axial symmetry, the $g$ values are correlated by the expression $G = (g_\parallel - 2)/(g_\perp - 2)$, which reflects the exchange interaction between copper(II) centres in the solid polycrystalline complex.[21] Accordingly, if $G > 4$, then the exchange interaction may be negligible; however, if $G < 4$, then the exchange interaction may be present, which is the case in the polymer complexes under investigation (see Fig. 1). Interestingly, in these complexes, $G < 4$, suggesting the presence of an exchange coupling and misalignment of the local tetragonal axes. The magnetic moments of these polymer complexes are normal at room temperature. The $G$ values follow the order

$$\mathrm{Cu(ligand)_2Cl_2 > Cu(ligand)_2Br_2 > Cu(ligand)_2(NO_3)_2}$$
$$\mathrm{> Cu(ligand)_2I_2}$$

This is consistent with the order of the strength of metal–anion interactions, i.e. chloride > bromide > nitrate > iodide. Our results are also in agreement with the respective positions of these anions as given in the spectrochemical series.[22]

**Table 5.** EPR parameter of the copper (II) polymer complexes **1**–**4**

| Complex | $g_\parallel$ | $g_\perp$ | $g_{iso}$ | $G$ | $\alpha^2$ | $A_\parallel \times 10^{-4}$ (cm$^{-1}$) | $A_\perp$ | $A_{iso} \times 10^{-4}$ (cm$^{-1}$) | $k_\parallel^2$ | $k_\perp{}^2$ | $k$ | $B$ | $\beta^2$ | $g_\parallel/A_\parallel$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 2.226 | 2.058 | 2.114 | 3.9 | 0.50 | 76.50 | 40.16 | 52.27 | 0.54 | 0.58 | 0.57 | 1.16 | 1.089 | 291 |
| **2** | 2.217 | 2.057 | 2.110 | 3.8 | 0.48 | 72.70 | 41.01 | 51.57 | 0.53 | 0.58 | 0.56 | 1.22 | 1.100 | 305 |
| **3** | 2.222 | 2.061 | 2.115 | 3.6 | 0.51 | 81.10 | 39.05 | 53.07 | 0.55 | 0.64 | 0.61 | 1.25 | 1.084 | 274 |
| **4** | 2.232 | 2.062 | 2.119 | 3.7 | 0.54 | 88.10 | 38.93 | 55.32 | 0.59 | 0.65 | 0.63 | 1.21 | 1.087 | 253 |

Approximate values of metal–ligand $\sigma$-bond coefficients $\alpha^2$ (defined as the fraction of unpaired electron density located on the copper ion) for these polymer complexes in the solid states were calculated from the optical absorption data using Eqn (2), where $\lambda = -829\ \text{cm}^{-1}$:

$$g_{\text{iso}} = 2.0023 - 4\lambda\alpha^2/\Delta E \qquad (2)$$

($\pi$-bonding effects were neglected). The $\alpha^2$ values (Table 5) for these polymer complexes indicate considerable covalency in the bonding between the copper(II) ion and the ligand. These values are comparable to those obtained in earlier studies.[1,2,4] The super-exchange splitting constant $A_{\parallel}$ was obtained semi-empirically, according to Pryce.[23]

The orbital reduction factors $k_{\parallel}$ and $k_{\perp}$ which are measures of the reduction of the spin–orbit coupling constant in these copper(II) polymer complexes, are obtained from Eqns (3) and (4):[24]

$$g_{\parallel} = 2.0023 - 8k_{\parallel}^2\lambda_0/\Delta_2 \qquad (3)$$

$$g_{\perp} = 2.0023 - 2k_{\perp}^2\lambda_0/\Delta_1 \qquad (4)$$

where

$$k^2 = (k_{\parallel}^2 + k_{\perp})/3 \qquad (5)$$

From the above relations, the orbital reduction factors ($k_{\parallel}$, $k_{\perp}$ and $k$), which are a measure of covalency,[24] can be calculated. In all cases $k_{\perp} > k_{\parallel}$, which is good evidence for the assumption of $^2B_{1g}$ as the ground state. For an ionic environment $k = 1$, and for a covalent environment $k < 1$; the lower the value of $k$, the greater is the covalent character.[25] Kivelson and Neiman[26] noted that, for an ionic environment, $g_{\parallel} > 2.3$ and for a covalent environment $g_{\parallel} < 2.3$. Theoretical work by Smith[19] seems to confirm this view. The $g_{\parallel}$ values reported here show considerable covalent bonding character. Further, the values are consistent with Cu–N and Cu–O-bonded copper(II) complexes. However, it is noteworthy that $k$ is regarded as a better measure of covalency than $g_{\parallel}$ and $\alpha^2$ values.

The in-plane and out-plane $\pi$-bonding coefficients ($\beta_1^2$ and $\beta^2$) are dependent upon the values of $\Delta E_{xy}$ and $\Delta E_{yz}$ in Eqns (6) and (7) (Table 4):[27]

$$\alpha^2\beta^2 = (g_{\perp} - 2.0023)\Delta E_{yz}/2\lambda_0 \qquad (6)$$

$$\alpha^2\beta_1^2 = (g_{\parallel} - 2.0023)\Delta E_{yz}/8\lambda_0 \qquad (7)$$

In this work, the copper(II) polymer complexes shows $\beta_1^2$ values indicating a moderate degree of covalency in the in-plane $\pi$-bonding; $\beta^2 > 1$ (Table 5) indicates the ionic character of the out-of-plane $\pi$-bonding.[28] All copper(II) polymer complexes have $G < 4$ (Table 5), indicating the occurrence of spin-exchange coupling[29] and that the ligand is strong field in nature.[30] The $g_{\parallel}/A_{\parallel}$ values (Table 5) show that the polymer complexes have octahedral geometry,[27] and this is further confirmed by the Symons plot.[31]

The data given in Table 5 indicate that (i) $\alpha^2$ shifts to higher values with increasing $g_{\text{iso}}$ (Fig. 3a), and $A_{\parallel}$ (Fig. 3b) $k_{\parallel}^2$ increase with increasing $g_{\parallel}$ (Fig. 4), and $k_{\perp}^2$ increasing with increasing $g_{\perp}$ (Fig. 5), as would be expected for electronegativity of axial position. In addition, Figures 3–5 show clearly that the shift is in the same direction to that of $g_{\text{iso}}$, $A_{\parallel}$, $g_{\parallel}$ and $g_{\perp}$.

The above results show clearly the effect of halogen groups on the EPR parameter on the stereochemistry of copper(II) polymer complexes. It is important to note that the existence of halogen groups enhances the electron density on the coordination sites and simultaneously increases the value of EPR parameters (Table 5).

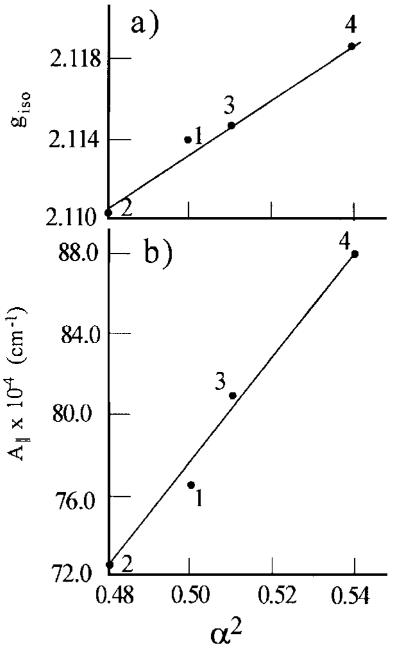


**Figure 3.** The relation between: (a) $g_{\text{iso}}$ and $\alpha^2$; (b) $A_{\parallel} \times 10^{-4}$ and $\alpha^2$.

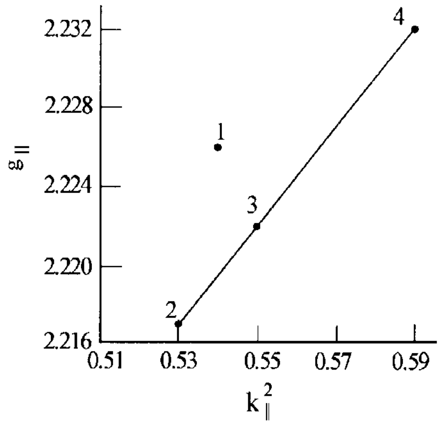


**Figure 4.** The relation between $g_{\parallel}$ and $k_{\parallel}^2$.

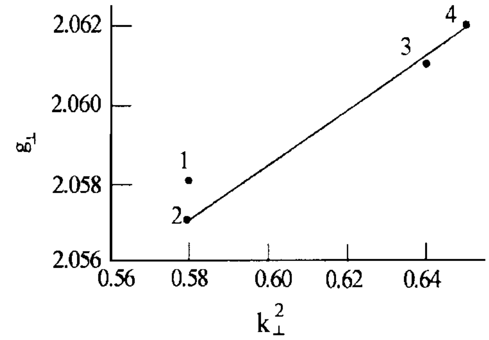


**Figure 5.** The relation between $g_\perp$ and $k_\perp^2$.

**Table 6.** Electronic spectral data and ligand field parameters of the complexes

| Complex | Spectral bands (obs.) ($cm^{-1}$) | $v_2/v_1$ | $\Delta_1$ | $\Delta_2$ | $\Delta_3$ |
|---|---|---|---|---|---|
| **5** | 18 975<br>22 860, 35 060<br>28 050 | 1.21 | 21 075 | 5085 | 4890 |
| **6** | 18 950<br>24 000, 34 890<br>29 890 | 1.27 | 21 650 | 6250 | 5590 |
| **7** | 20 150<br>24 170, 35 100<br>28 910 | 1.20 | 22 250 | 5220 | 4440 |
| **8** | 19 660<br>23 600, 34 980<br>29 220 | 1.13 | 21 760 | 6040 | 4420 |
| **9** | 29 890<br>31 950, 39 350 | 1.07 | 31 990 | 3260 | 7100 |
| **10** | 19 560<br>24 380, 34 660<br>29 290 | 1.25 | 21 660 | 6020 | 4610 |
| **11** | 19 540<br>24 200, 34 860<br>29 280 | 1.24 | 21 640 | 5860 | 4780 |
| **12** | 19 450<br>24 200, 34 680<br>29 190 | 1.24 | 21 550 | 5950 | 4690 |

## Geometry of the $Pd^{2+}$–$Pt^{2+}$ polymer complexes

With the exception of a small number of palladium derivatives, few six-coordinate complexes of these species are known. The majority of complexes are four-coordinate and square planar. The solid reflectance spectra of these polymer complexes exhibit bands characteristic of square-planar palladium(II) polymer complexes.[3] Three d–d spin-allowed transitions are expected according to the transitions from the three low-lying d-levels to the empty $d_{x^2-y^2}$ orbitals. The ground state is $^1A_{1g}$, and the excited states corresponding to these transitions are $^1A_{2g}$, $^1B_{1g}$ and $^1E_g$ in order of increasing energy. The transition energies are determined as follows:

$$b_{2g} \rightarrow b_{1g} = \Delta_1 - C \qquad (8)$$

$$a_{1g} \rightarrow b_{1g} = \Delta_1 + \Delta_2 - 4B + C \qquad (9)$$

$$e_g \rightarrow b_{1g} = \Delta_1 + \Delta_2 + \Delta_3 - 3B - C \qquad (10)$$

The electronic spectra of palladium complexes show $^1A_{1g} \rightarrow {}^1A_{2g}$ (30 150–19 660 $cm^{-1}$), $^1A_{1g} \rightarrow {}^1B_{1g}$ (24 200–22 860 $cm^{-1}$) and $^1A_{1g} \rightarrow {}^1E_g$ (29 290–28 050 $cm^{-1}$).

The values of ligand field parameters $\Delta_1$, $\Delta_2$ and $\Delta_3$ were calculated using various energy-level diagrams. These consist of the values reported earlier for such complexes.[32]

The electronic spectra of the platinum complexes exhibit bands characteristic of a square-planar arrangement around the metal atom.

The values of ligand parameters $\Delta_1$, $\Delta_2$ and $\Delta_3$ were calculated as mentioned above for palladium(II) complexes (Table 6). The $\Delta_1$ values for platinum(II) complexes are much higher than those observed for palladium(II) complexes, but they are in accordance with those required for platinum(II) square-planar complexes. The values of $\Delta_1$ lie in between those observed for cyanide (~30 000 $cm^{-1}$) and chloride complexes (~19 000 $cm^{-1}$) and are consistent with intermediate ligand strength.[32]

## Mode of coordination of an acid amide group

The free acid-amide has a planar structure with a resonance stabilization energy.[33] The amide-nitrogen coordination without deprotonation will change the $sp^2$ hybridization of the nitrogen atom into an $sp^3$ hybridization with loss of the stabilization energy, as well as loss of the planar structure. On the other hand, the amide-oxygen coordination will require only the donation of a lone pair electron to a metal without change in hybridization and loss of the resonance energy. Therefore, oxygen coordination is more favoured than nitrogen coordination for non-deprotonated acid-amide groups. The results of this study, as well as our previous results[11] for various acid-amide complexes, support the above scenario.

Hughes and Rutt[34] studied the copper(II) complexes of 2-acetamidothiazole and benzothiazole and concluded that the non-deprotonated amide-nitrogen atoms are coordinated to copper(II). The evidence they presented, however, seems to be insufficient in view of our discussions above, as they found an increase in the intensity of $\nu$(N–H) of the amide groups and a shift of the amide I band to a lower frequency; however, a similar change on coordination for $[Pd(APH)_2Cl_2]$, in which APH is coordinated only through the pyridine ring-nitrogen atom without coordination of an amide group, was found by us.

The spectra of the nitrato complexes show various bands at *ca* 1255, 1030 and 825 cm$^{-1}$ consistent with the monodentate nature of the nitrate group.

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