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Single-Crystal Polarized Electronic and Electron Spin Resonance Spectra of the Trigonal-Bipyramidal Complex Aquobis(1,10-phenanthroline)copper(II) Nitrate

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Received December 1, 1976 AIC60860Y

The single-crystal polarized electronic and electron spin resonance spectra of the trigonal-bipyramidal complex aquobis(1,10-phenanthroline)copper(II) nitrate have been recorded. The crystals are monoclinic, and the copper atom possesses C_2 site symmetry. By recording four couples of electronic spectra, on different crystal faces, we were able to determine the directions of maximum polarization in the *ac* plane, yielding both the principal directions and values of the ϵ tensor. The order of the electronic transitions was found to conform to ligand field predictions, in contrast with previous findings in similar chromophores. Angular overlap calculations reproduced nicely the energies of the electronic transitions and the directions and values of the magnetic tensor, but the values of the parameters were found to be at variance from those expected on the basis of chemical considerations.

Introduction

After the success in the interpretation of the spectral properties of cubic transition metal complexes obtained with ligand field models,[1] the interest of many spectroscopists has shifted, in the last years, toward low-symmetry coordination compounds,[2] and several single- crystal studies have been reported. The main reason for this is that most of the transition metal complexes of biological interest are often found in highly distorted environments.[3] This kind of investigation requires a search for adequate theoretical models which can provide a key to interpret the spectral properties, and several attempts have been made to extend the ligand field formalism to low-symmetry chromophores,[4-9] in general yielding satisfactory results, although often not as good as in cubic complexes.

Another problem to be faced in the study of low-symmetry complexes is that, when a coordination compound does not possess axial or rhombic symmetry, group theory cannot determine which are the principal directions of the tensors which describe the electronic properties of the complex, such as the absorption ellipsoid, ϵ, which is relevant in the interpretation of the electronic spectra, the **g** and **A** tensors of the spin Hamiltonian to interpret the ESR spectra, etc. Often an idealized symmetry has been assumed in order to fix the directions of the principal axes of the different tensors, and the axes of the different tensors have been considered parallel to each other. Only in the last years it has become clear in the chemical literature that the **g** and **A** tensors can be nonparallel,[10-12] and the correct formulas for the interpretation of the ESR spectra have been worked out. Finally, quite recently, Hitchman has shown,[13] using an indirect mathematical procedure, for unit cells containing crystallographically nonequivalent chromophores, that the magnetic and the molecular axes, i.e., the principal directions of ϵ, can be nonparallel to each other.

We have now studied the single-crystal linearly polarized electronic and the ESR spectra of $[Cu(phen)_2H_2O](NO_3)_2$ (phen is 1,10-phenanthroline). This complex crystallizes in the *C*2/*c* space group,[14] and the copper atom possesses C_2 site symmetry, so that all the vectors defined on one molecule are parallel to the corresponding ones of the other three molecules in the unit cell. The crystals appear, therefore, to be well suited for determining the principal directions of the **g** and ϵ tensors, without making any assumption regarding the molecular axes. Further, the complex is trigonal bipyramidal, and the interpretation of the electronic properties of these complexes is not well settled in the literature. In general there is now agreement[5] that in $[CuCl_5]^{3-}$, $[CuX(Me_6tren)]^+$ (X = Cl, Br; Me_6tren is tris(dimethylaminoethylamine)), etc. the order of the levels is $^2A_2' < {}^2E' < {}^2E''$, in the notation of D_{3h} symmetry, and this is confirmed by ligand field calculations. However a different ordering has been proposed for $Cu(NH_3)_2Ag(SCN)_3$ and $[CuI(bpy)_2]I$ (bpy is 2,2′-bipyridine),[16] on the basis of single-crystal electronic spectra, but no explanation has been provided for this behavior. The close similarity of the present complex to the bipyridine complex studied by Hathaway and its relatively high symmetry inclined us to think that its polarized spectra could provide useful information on the order of the electronic levels in trigonal-bipyramidal copper(II) complexes.

Experimental Section

The title compound was prepared as previously described[17] and single crystals were grown by slow evaporation of water–methanol solutions. Weissenberg techniques confirmed that the crystals conform to the structure report:[14] space group *C*2/*c*, $a = 2258$, $b = 723$, $c = 1659$ pm; $\beta = 123.6°$; $Z = 4$. The shape of the crystals was in general not regular, the most developed face being $(10\bar{1})$. In some crystals also the (001) face was well formed, and on both of them it was possible to record electronic spectra with the apparatus previously described.[18] From suitable crystals sections were made perpendicular to the main $(10\bar{1})$ face, yielding the (010) and the (209) faces.

ESR spectra were recorded with the apparatus previously described.[19]

In the calculations the angular overlap model (AOM) was used with the matrices reported by Schäffer.[20] In the case of the nitrogen donor atoms it was considered that an e'_π contribution different from zero is possible only in a direction which is perpendicular to the aromatic ring. Using the experimental coordinates[14] the ratios ${e'_{\pi_s}}^{N(1)}/{e'_{\pi_c}}^{N(1)} = 0.15$ and ${e'_{\pi_s}}^{N(2)}/{e'_{\pi_c}}^{N(2)} = 0.02$ have been evaluated. For the sake of simplicity it was assumed ${e_{\pi_s}}^{O} = {e_{\pi_c}}^{O}$, since quite similar values for these parameters have been previously calculated.[21] The energies of the transitions were fit allowing the parameters to vary on a very large range of values and increasing the number of points in the region where promising values for the transitions were found.

The *g* principal values and directions were calculated using the eigenfunctions obtained from the calculations of the electronic energy levels. The procedure followed in this calculation was quite similar to that suggested by Belford et al. for other low-symmetry chromophores.[22] In the present case, the main difference was that the coefficient of d_{z^2} in the ground state was not considered small as compared to the coefficients of the other functions of the ground state.

Results and Discussion

ESR Spectra. The room and liquid-nitrogen temperature powder spectra show only a very broad, apparently isotropic, spectrum with a *g* value of 2.089. The single-crystal spectra show one principal *g* value, g_3, parallel to the C_2 crystal axis. The spectra obtained by rotating around this direction gave the other two principal *g* values, g_1 and g_2 (Table I), and their directions, which are shown in Figure 1. Owing to the favorable orientation of the molecules in the unit cell the crystal *g* values are the molecular *g* values and intermolecular exchange interactions, if present, are expected to affect only the line width and not the *g* values. The g_1 direction, corresponding to the lowest *g* value, corresponds quite closely to the would-be

Table I. Experimental and Calculated **g** Tensor for the Complex $[Cu(phen)_2H_2O](NO_3)_2$

	Principal values		Calcd principal directions in the g_1g_2 plane[b]
	Exptl	Calcd[a]	
g_1	2.022 ± 0.002	2.02	96.8
g_2	2.125 ± 0.003	2.12	6.8
g_3	2.227 ± 0.008	2.23	

[a] The calculations were performed using the experimental energies for the excited states and the value $\zeta = -450$ cm^{-1} for the spin-orbit coupling constant of the copper atom. [b] Degrees from the experimental g_2 direction toward g_1 (Figure 1).

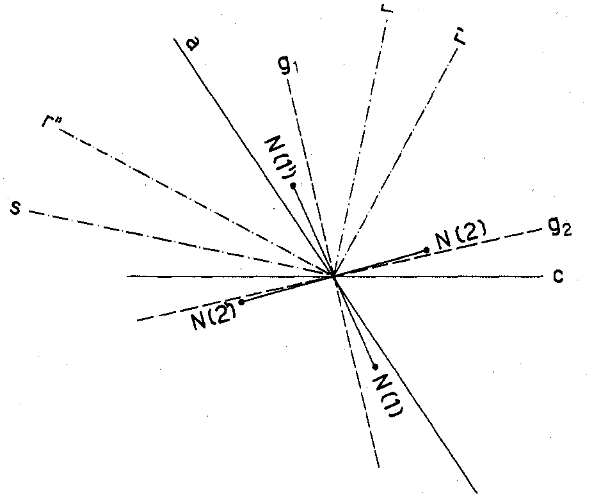


Figure 1. A projection of the molecule in the *ac* plane. The copper and the oxygen from the coordinated water are not shown for clarity purposes. They should be in the origin of the coordinates. *a*, *r*, *r′*, *s*, and *r″* are the directions along which the polarized electronic spectra were recorded. The principal directions of the g tensor are indicated by g_1 and g_2. *a*, *r*, *r′*, *s*, *r″*, g_1, and g_2 lie in the *ac* plane.

C_3 symmetry axis of the trigonal bipyramid, and g_2 is almost coincident with the projection of the Cu–N(2) and Cu–N(2′) bond directions on the *ac* plane. The *g* values of the present complex are much different from those of $[CuI(bpy)_2]I$[16] and reflect better the large anisotropy in the equatorial plane of the trigonal bipyramid. The value of g_3, in the copper–oxygen bond direction is larger than that in the copper–iodine bond direction of $[CuI(bpy)_2]I$ (2.227 against 2.16), perhaps as a consequence of the different nephelauxetic properties of the two donors. As a matter of fact the g_2 and g_3 values of the present compound are quite similar to those of the cis octahedral $[Cu(NO_2)(bpy)_2]^+$,[23] where NO_2 is acting as a bidentate ligand, making the overall coordination geometry not too distant from a trigonal bipyramid.

Another interesting remark is that the ESR lines are very broad and this is the reason that the powder spectrum simulates an isotropic situation. The maximum peak-to-peak width, about 0.05 *T*, is observed parallel to the g_3 direction and is almost two times that observed in the other two directions. The origin of this behavior may be due to the close proximity of the protons of the water ligand, which presumably undergoes some kind of free rotation. Similar effects had been previously observed for nickel–ammonia complexes.[24]

Electronic Spectra. The single-crystal electronic spectra were recorded on the (10$\bar{1}$), (001), (010), and (209) faces with the directions of the polarizer corresponding to the extinction directions, which are shown in Figure 1. The corresponding spectra are shown in the Figures 2 and 3. The spectrum along *b*, which yields the *z* component of the molecular spectrum, shows one very intense absorption maximum centered at 12 × 10^3 cm^{-1} and a shoulder at about 15 × 10^3 cm^{-1}. The spectra recorded in the *ac* plane reflect the anisotropy of the molecular *xy* plane. They show in general the presence of two peaks, at (12.5–13) × 10^3 cm^{-1} (1) and 15 × 10^3 cm^{-1} (2), of different intensities. The high-frequency band appears to be of lower intensity. If the ratio between the intensities of these two peaks in every particular spectrum, $I(2)/I(1)$, is assumed as a measure of the degree of polarization, it is possible to guess the directions of maximum polarization in the *xy* plane. It is apparent that the ratio is maximum for the *r* spectrum, while it is smaller for the *a* spectrum, and even smaller for the *r′* one, suggesting that the *r* direction is the closest one to one of the principal directions of the ϵ tensor in the *xy* plane, followed by the *a* and *r′* directions. If *r* corresponds to the ϵ_x axis the *r′* spectrum should be more polarized than the *a* spectrum, and this is contrary to the experimental result. It is apparent now that the ϵ_x axis must be rotated from *a* towards g_1. Locating the ϵ_x axis parallel to g_1 would require equivalent *a* and *r* spectra, again in contrast with the experimental result. Therefore, the most probable direction of the ϵ_x axis seems to be in a range of 5–10° from g_1 toward *r*. With this assumption the least value for $I(2)/I(1)$ is expected for the spectrum along the *s* direction, as observed. Attempts were also made to use a quantitative procedure similar to the one suggested by Hitchman.[13] The main difference from his procedure was that we used four couples of spectra, therefore obtaining a homogeneous system of four equations with the four unknowns ϵ_{xx}, ϵ_{yy}, ϵ_{zz}, ϵ_{xy}, allowing the determination of their ratios. Finally diagonalization yielded the principal directions. The directions were found to be dependent on the wavelength chosen, yielding, for instance, the values (degrees from the g_1 direction toward the *r* one): 8° at 12.4 × 10^3 cm^{-1}, 12° at 13 × 10^3 cm^{-1}, and 25° at 15

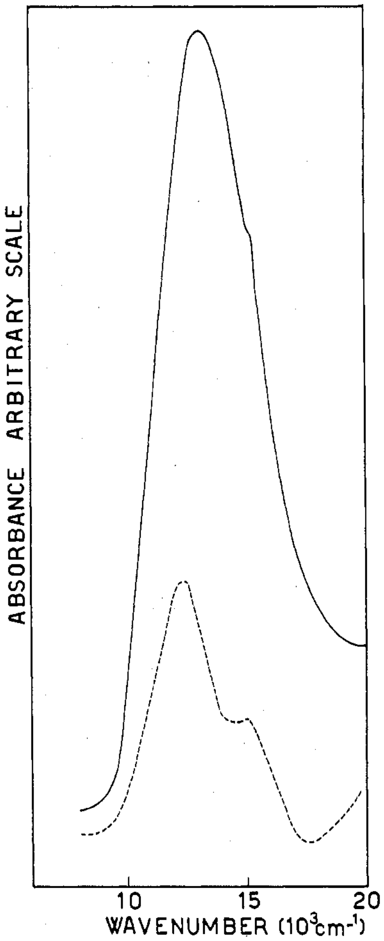


Figure 2. Single-crystal polarized electronic spectra recorded at 77 K on the (010) face: —, electric vector parallel to *r″*; ---, parallel to *r′*.

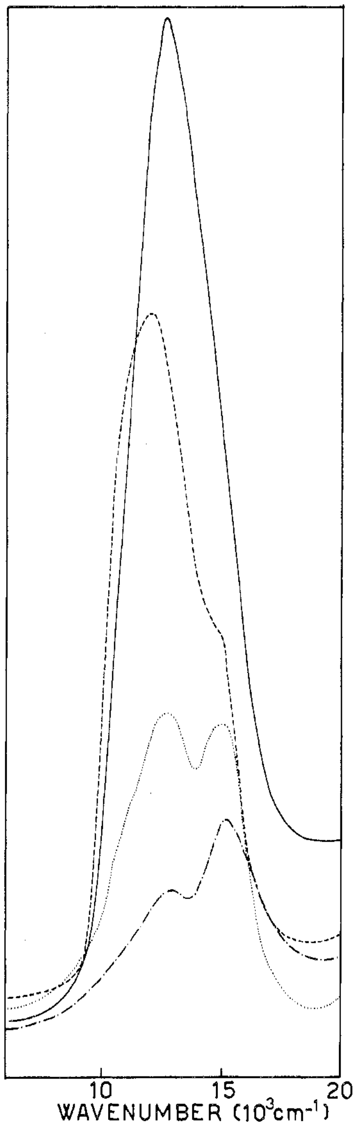
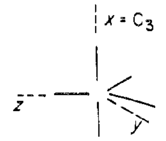


Figure 3. Single-crystal polarized electronic spectra recorded at 77 K on the (10$\bar{1}$), (001), and (209) faces. Since all the couples of spectra contained the *b* spectrum, they have been drawn in scale: —, electric vector parallel to *s*; ---, parallel to *b*; ···, parallel to *a*; -·-·-·, parallel to *r*.

$\times 10^3$ cm^{-1}. On these figures a percent error of about 10% can be estimated.[13] It is probable, however, that stray light affecting the zero line of the spectra makes less reliable the value corresponding to the less intense peak, owing to the larger percent error in the observed absorbances. It is apparent, however, that the values for 12.4 and 13 $\times 10^3$ cm^{-1} correspond quite closely to the values indicated by our qualitative analysis.[25] We feel confident to conclude that in the present case the molecular axes are quite close to the magnetic ones, although they may well be not coincident.

The electronic transitions can now be assigned. First of all it is apparent that the *z* and *y* spectra are quite similar as regards the positions of maxima (12 and 13 $\times 10^3$ cm^{-1}, respectively) and intensities of the transitions, while the *x* spectrum is different and shows only one main peak at 15 $\times 10^3$ cm^{-1} of far lower intensity. Since the *x* direction is close to the direction of the would-be C_3 axis of the trigonal bipyramid, it appears that the spectra can be interpreted, at least in first approximation, using the D_{3h} selection rules. With a $^2A_1'$ ground level the $^2A_1' \rightarrow {}^2E'$ transition is allowed in the plane perpendicular to the C_3 axis (corresponding to our *yz* plane), while the $^2A_1' \rightarrow {}^2E''$ transition is forbidden. On the basis of the polarizations and of the intensities of the transitions it seems reasonable to assign the more intense bands, at 12 and 13 $\times 10^3$ cm^{-1}, to the split components of the $^2A_1' \rightarrow {}^2E'$ of D_{3h} symmetry and the less intense band at 15 $\times 10^3$ cm^{-1} either to one of the two components of $^2A_1' \rightarrow {}^2E''$ or to both of them lying quite close in energy. The nonzero intensity of the high-frequency band can be brought about by the actual low symmetry of the chromophore. As shown below, the $^2A_1' \rightarrow {}^2E''$ transition is allowed in C_{2v} and C_2 symmetries. In this latter symmetry the $^2A \rightarrow {}^2A$ transition is *z* polarized and therefore we assign the 12 $\times 10^3$-cm^{-1} band to the A component of the split E′ level, and the 13 $\times 10^3$-cm^{-1} band to the B component.



D_{3h}	C_{2v}	C_2
$A_1' \rightarrow E'(z,y)$	$A_1 \rightarrow A_1(z)$	$A \rightarrow A(z)$
E''(no)	$B_2(y)$	$B(x,y)$
	A_2(no)	$A(z)$
	$B_1(x)$	$B(x,y)$

The present assignment is far different from that of [CuI(bpy)$_2$]I[16] and resembles closely those of $CuCl_5^{2-}$ etc.[15] as regards the relative energies of the excited E levels. On the other hand also the polarized spectra of the present compound did not look much like those of [CuI(bpy)$_2$]I. It is somewhat surprising that apparently similar chromophores can yield completely different results.

The suggested ordering of the levels conform to the predictions of simple ligand field models. An attempt was made to put the assignment on a more quantitative basis, by using the angular overlap model (AOM).[20] The main reason for using this model is that it allows for metal–donor interactions possessing a symmetry different from cylindrical, a condition which seems important for the phenanthroline ligand. Previous attempts to use the AOM to calculate the energies of trigonal–bipyramidal copper(II) complexes including only e'_σ parameters did not yield satisfactory results on a quantitative basis.[26] Similar calculations in the present case, assigning the 12 $\times 10^3$-cm^{-1} band to $d_{z^2} \rightarrow d_{xy}$, the 13 $\times 10^3$-cm^{-1} band to $d_{z^2} \rightarrow d_{x^2-y^2}$, and the 15 $\times 10^3$-cm^{-1} band to $d_{z^2} \rightarrow (d_{xz},d_{yz})$, yielded $e'^{\,N(2)}_\sigma = 2.67$, $e'^{\,O}_\sigma = 1.33$, and $e'^{\,N(1)}_\sigma = 6.67 \times 10^3$ cm^{-1}. These values do not seem to be meaningful, since $e'^{\,N(2)}_\sigma$ and $e'^{\,O}_\sigma$ are really too low, and $e'^{\,N(2)}_\sigma$ and $e'^{\,N(1)}_\sigma$ are too different from each other.

With the aim to check if a more complete model could reproduce the energies of the observed transitions we introduced also π effects and took into account the angular distortions of the chromophore, according to the scheme shown in the Experimental Section. A reasonable fit of the experimental transitions was found for the range of values of the parameters shown in Table II. It is apparent that also the inclusion of π effects and angular distortion cannot lead to chemically acceptable values of the parameters. If one manages to have reasonable values for the nitrogen donors, the values for oxygen are too low. As a matter of fact if for oxygen the K_σ and K_π values reported by Hitchman are used,[21] no fit of the transitions can be obtained.

With the eigenvectors corresponding to the best fit of the electronic transitions, we calculated then the principal *g* values and directions using the procedure outlined in the Experimental Section. In order to reduce the number of new parameters to a minimum we assumed isotropic *k* and ζ. The calculated *g* values and their directions are shown in Table I. The accord with the experimental values is quite satisfactory. In particular the large difference between the g_1 and g_2 values, which should

Table II. Assignment of the Absorption Maxima to the Electronic Transitions of the Complex $[Cu(phen)_2H_2O](NO_3)_2$[a]

Transition[b]	Obsd	Calcd[c]
$^2A(^2A_1') \rightarrow {}^2A(^2E')$	12	11.4-11.7
$^2B(^2E')$	12.8	12.9-13.4
$^2B(^2E'')$		14.9-15.3
$^2A(^2E'')$	15	15

[a] All the values are expressed in 10^3 cm^{-1}. [b] The energy levels are labeled according to the C_2 symmetry group; in parentheses are the symmetry labels of the D_{3h} symmetry group. [c] $e'_{\sigma}{}^{O} = 0.95 \pm 0.05$, $e'_{\pi_s}{}^{O} = e'_{\pi_c}{}^{O} = -0.25$, $e'_{\sigma}{}^{N(1)} = 6$, $e'_{\pi_c}{}^{N(1)} = 0.15 \pm 0.1$, $e'_{\sigma}{}^{N(2)} = 5.4$, $e'_{\pi_c}{}^{N(2)} = (1.3 \pm 0.2) \times 10^3$ cm^{-1}, $e'_{\pi_s}{}^{N(1)}/e'_{\pi_c}{}^{N(1)} = 0.15$, $e'_{\pi_s}{}^{N(2)}/e'_{\pi_c}{}^{N(2)} = 0.02$.

correspond to the $g_{\perp}$ value of pure D_{3h} symmetry, can be easily reproduced as a consequence of the ground-state eigenfunction. This suggests that, although the values of the fitting parameters may not be satisfactory to a chemical sense, they can however reproduce nicely the experimental observables. The chemical meaning of the ligand field parameters is an open problem,[27] and particularly in the case of the copper(II) complexes it is not uncommon to find values of the parameters which do not appeal to the chemical sense[28] but are however useful, at least in a bookkeeping sense, to interpret the spectra.

Conclusions

In the present work accurate experimental techniques allowed the determination both of the principal values and directions of the **g** and ϵ tensors. Contrary to the findings of Hitchman[13] the two tensors were not found appreciably misaligned.

Although the number of experimental data was large, it was not sufficient to determine the values of the parameters of the AOM, and some additional assumptions had to be made. This result is quite general, and although recently the use of the magnetic parameters (**g**, χ, etc.) has been advocated,[29] it appears that the determination of the parameters can be obtained only by introduction of ad hoc assumptions (ζ and k isotropic, etc.).

An important result of our calculations is that no fit of the experimental data could be obtained transferring the values of the parameters from different complexes,[21] a fact that had not happened for other low-symmetry chromophores[30] but which seems now to be fairly general for trigonal-bipyramidal copper(II) complexes.

Acknowledgment. Thanks are due to Professor L. Sacconi and to Professor I. Bertini for helpful discussions.

Registry No. $[Cu(phen)_2H_2O](NO_3)_2$, 57572-96-0.

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Circular Dichroism of Copper and Nickel Tetra- and Pentapeptide Complexes

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Received January 21, 1977 AIC70052M

Asymmetric centers located one or two amino acid residues beyond the planar chelate ring structure in copper(II) and nickel(II) oligopeptide complexes still contribute to the visible circular dichroism of the metal ion chromophore. The triply deprotonated tetrapeptide complexes of A_4, V_4, G_3A, and G_3AOCH_3 and pentapeptide complexes of A_5, G_4A, and G_4AOCH_3 (where G is glycine, A is L-alanine, V is L-valine, and OCH_3 is the methyl ester) are compared with the CD behavior of tripeptide complexes. Intramolecular hydrogen bonding and weak axial coordination are proposed to account for the required vicinal interactions between the metal ion center and the asymmetric centers in the fourth and fifth amino acid residues in the peptides. The metal ions increase the rates of hydrolyses of the pentapeptide esters but do not affect the tetrapeptide esters. The CD spectra of copper(III) and nickel(III) oligopeptide complexes also are reported.

Introduction

The circular dichroism (CD) of copper(II) and nickel(II) complexes with optically active di- and tripeptides has been studied.[1-5] In the present work we address the question of what happens to the visible CD spectra in complexes of tetrapeptides, pentapeptides, and their methyl esters as the optically active center is moved down the peptide chain away from the site of chelation to these metal ions. Circular dichroism in the complexes arises from the vicinal interaction of the metal ion chromphoric center and the carbon atom asymmetric center in the peptide residue. Therefore, the CD signal would be expected to decrease sharply as these two centers are separated. Nevertheless, we find significant CD signals for Cu(II) and Ni(II) complexes even when the optically active center is five atoms away from the metal ion (in terms of the square-planar coordination sites). Thus, when the carbon atom next to $R_{(5)}$