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Electronic and Bonding Properties of (Polyamine)copper(II) Complexes Studied by Experimental and Quantum-Chemical Methods

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Five copper(II) chelates of polyamine ligands, being potential precursors for the synthesis of magnetic dimers, have been synthesized and characterized. Various physicochemical and spectroscopic studies (viz., infrared, near-infrared, and visible reflectance, electron spin resonance, and magnetic susceptibility studies as well as molecular conductivity determinations) have been carried out to throw light on the structural features of the compounds. Depending on the nature of both the polyamine ligand (en, trien, tetren, bpy) and the counteranion (PF_6^-, ClO_4^-), the complexes exhibited different stereochemistries, which are dominated by five- and six-coordinate geometries with some degree of distortion from the regular ones. These geometries are present in the structural pathway established for copper(II) polyamine complexes. An insight concerning the ground-state electronic structure and related properties of these compounds was gained through EHMO calculations performed on model compounds possessing regular geometries in the structural pathway. Accordingly, the σ character of the covalent bonding, the relative strength of the coordination bonds, and the reactivity of the compounds toward nucleophilic substitution reactions have been verified. Furthermore, within this framework, the EPR and electronic spectral data of the compounds were interpreted. The calculated $g_{\parallel}$ and $A_{\parallel}$ values were in good agreement with those derived experimentally. The electronic absorptions observed for the (aliphatic polyamine)copper(II) chelates are confidently assigned to LMCT and ligand field transitions. Intraligand transitions were observed only in the case of the bpy complex and were characterized on the basis of EHMO calculations performed on the free ligand as well.

Introduction

We recently engaged in the investigation of the magnetic exchange interactions propagated through multiatom bridges in new d^9–d^9 exchange-coupled magnetic systems using experimental and quantum-chemical methods. Our main interest has been focused on the theoretical prediction and the experimental confirmation of the effect of structural and bonding parameters of magnetic centers and extended bridging species, on the strength and nature of the magnetic interactions. To accomplish this, full understanding of the structural and bonding properties of both the precursor mononuclear complexes and the extended bridging species forming the magnetic dimers was necessary as a first step.

The wide range of stereochemistries exhibited by copper(II) ion in its coordination compounds with polyamine ligands make these complexes good candidates to be used as precursors for the aforementioned purpose. Copper(II) mononuclear complexes with polyamine ligands have been extensively studied both theoretically and experimentally.[2-12]

Attempts have been made to correlate their versatile stereochemistries with the electronic properties of the copper(II) ion by means of EPR, optical spectra, and magnetic susceptibility measurements. A convenient electronic criterion of stereochemistry along with a structural pathway representing the sense of distortions present and the variation of the EPR and electronic spectra in this series of complexes have been established.[2] Moreover, the treatment of the covalence properties of these compounds by EPR studies[2a,5c,6b,c,11] according to the criteria established by Maki and McGarvey[13] was very important. However, to our knowledge, the electronic and bonding properties of the copper(II) polyamine complexes have not been studied by quantum-chemical methods, so far.

In this paper we report the experimental results concerning the structure and bonding of a series of new polyamine copper(II) complexes, exhibiting five- and six-coordinate geometries in the framework of the structural pathway established for Cu(II) polyamine complexes. The complexes studied corresponded to the formulas $[Cu(en)_2(OH_2)(FPF_5)](PF_6)$, $[Cu(trien)(FPF_5)](PF_6)$, $[Cu(tetren)(FPF_5)](PF_6)$, $[Cu(tetren)](ClO_4)_2$, and $[Cu(bpy)_2(NO_3)](PF_6)\cdot H_2O$ (where en, trien, tetren and bpy are the abbreviations used for the ethylenediamine, triethylenetetramine, tetraethylenepentamine, and 2,2′-bipyridine ligands, respectively). Furthermore, the results of a systematic investigation of the ground-state electronic structure and related properties of the compounds, within the framework of extended Hückel LCAO–MO calculations performed on model complexes possessing regular geometries in the structural pathway are presented.

Experimental and Theoretical Section

Preparation of Complexes. All complexes were prepared by using known procedures[6b,c,14,15] and gave satisfactory elemental analyses (Table I).[16]

Magnetic Measurements. Magnetic measurements were carried out on polycrystalline samples with a Faraday-type magnetometer equipped with a Cahn RG-HV electrobalance. The applied magnetic field was 0.625 T. Mercury tetrakis(thiocyanato)cobaltate(II) and the complex $[Ni(en)_2]S_2O_3$ were used as susceptibility standards.[17] Corrections for diamagnetism of the complexes were calculated from Pascal's table.[17] The TIP per copper ion was assumed to be 60×10^{-6} cm^3 mol^{-1}.

EPR Measurements. EPR powder spectra were measured at room temperature and in some cases at −120 °C on a JES-ME-3X spectrometer in the X-band at ν = 9.30 GHz.

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Table II. The Most Relevant Infrared and Reflectance Spectral Bands (cm^{-1}) of the Solid Compound Along with Their Assignments[a]

$[Cu(en)_2](PF_6)_2 \cdot H_2O$	$[Cu(trien)](PF_6)_2$	$[Cu(tetren)](PF_6)_2$	$[Cu(tetren)](ClO_4)_2$	$[Cu(bpy)_2(NO_3)](PF_6) \cdot H_2O$	assgnt
IR					
404 w	375 w	410 w		263 w	ν(Cu–N)
				296 w	
554 s	555 s	556 vs		554 vs	ν(F–P–F)
			628 s		ν(O–Cl–O)
830 vs	835 vs, br	845 vs, br		843 vs, br	ν(P–F)
880 m, sh	890 m, sh	890 m, sh			
			1095 vs, br		ν(Cl–O)
				1307 vs	$\nu_s(NO_3)$
				1465 vs	$\nu_{as}(NO_3)$
Near-IR					
4950 m	4940 m	4950 m	4920 m		2ν(C–H)
5280 m	5271 w	5283 w	5236 w	5271 w	
5858 w	5811 w	5794 w	5784 w		
5999 w	5959 w	5942 w	5914 w	6068 m	
6477 m	6431 m				2ν(N–H)
6530 m	6490 m	6510 m	6490 m		
6570 m	6550 m	6560 m			
7112 w					
7246 sh				7246	$2\nu(H_2O)$
UV–Vis					
12820 sh	12770 sh	12770 sh	12760 sh	10710	
15870 sh	15150 sh	15267	15220	13890	d–d
18180	17920			15770 sh	
41490	38310	36630	36765	23530 sh[b]	LMCT

[a] w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder. [b] This complex showed in addition bands at 25 320 sh, 28 740 sh, 32 260, 33 670, 39 520 sh, 40 650, and 47 170 sh, which are assigned as n → π* and π → π* intraligand transitions located on the bpy and NO_3^- ligands.

Optical Measurements. Reflectance spectra have been measured in the range 200–2000 nm on a Beckman UV 5240 spectrometer by using Nujol films. We used Sr_2ZnTeO_6 and freshly sintered MgO as standards. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer (4000–250 cm^{-1}) using KBr pellets.

Conductivity Measurements. Molar conductivities for solutions 10^{-3} M in methanol (or nitromethane for the bpy complex) were measured at 25 ± 0.002 °C with a Beckman Model PC-18A conductance bridge, using a frequency of 3000 Hz.

Computational Details. Calculations were carried out in the framework of the extended Hückel LCAO–MO method,[18] with off-diagonal matrix elements given by the expression of Wolfsberg–Helmholz,[19] by use of the FORTICON-8 computer program.[20] Although the three options offered by the FORTICON-8 program were tested, the best results were obtained by using option 0. On the contrary, options 2 and 3 presented serious charge convergence problems, probably due to the large basis sets used. In order to overcome these problems the size of the basis sets was reduced by using hypothetical nitrogen donor atoms possessing only one sp^3-hybridized orbital. The results were in accordance with those obtained by option 0 concerning the ordering of the MO's. Since these results did not fully describe the electronic structures of the real molecules, only those obtained by option 0 were used for our purposes. To have reasonable diagonal matrix elements that allow for a good fit between experimental and theoretical ligand field transitions of the compounds, we determined the appropriate H_{dd} and K values following a series of calculations. The deviations between the theoretical and experimental frequencies of the ligand field bands plotted against the H_{dd} and K values showed characteristic minima, which correspond to the best values of the two parameters ($H_{dd} = -12.92$ eV and $K = 1.78$ for all complexes). The values of all other diagonal matrix elements H_{ii}, for carbon, nitrogen, sulfur, oxygen, and hydrogen were those given in the literature.[18,20] Orbital exponents for nitrogen, carbon, oxygen, sulfur, and hydrogen were those used[18] previously. The basis set of valence AO's for Cu consisted of 3d, 4s, and 4p, with the last two being single Slater-type orbitals, whereas the 3d functions were considered as contracted linear combinations of two Slater-type functions. The exponents of the two d AO's were taken as 5.95 and 2.30 with corresponding relative weights of 0.593 32 and 0.574 42. The 4s and 4p exponents for Cu were taken as 2.05 and 1.325, respectively.

Due to the lack of X-ray crystal data for our complexes the structural parameters were derived from analogous copper(II) polyamine complexes of known structures resembling closely the structures of the compounds cited. Moreover, the geometries were selected to represent the regular structures present in the structural pathway and to assure symmetries allowing for the theoretical calculation of the EPR parameters according to well-established expressions. The regularized geometries of the selected model compounds were taken from the crystal structures of the $Cu(en)_2(SCN)_2$, $[Cu(trien)(SCN)]^+$, $[Cu(tren)(NCS)]^+$, and $[Cu(bpy)_2(NO_2)]^+$ complexes possessing elongated tetragonally distorted octahedral (D_{2h}),[21] square-pyramidal (C_{2v}),[22] trigonal-bipyramidal (D_{3h}),[23] and cis-octahedral (C_{2v})[24] stereochemistries, respectively. In order to overcome the convergence problems for the bpy complex owing to its very large basis set, we used four hypothetical nitrogen donor atoms substituting for the two bpy ligands. For each nitrogen donor atom only one sp^2 hybrid orbital directed to the central atom was considered. For this hypothetical $[Cu(N_{sp^2})_4(NO_3)]^+$ complex the diagonal matrix elements H_{ii} for the sp^2 hybrid orbitals were obtained by EHMO–SCCC calculations on the free bpy ligand. Moreover, in the final calculation all H_{ii} values used were the converged ones in the EHMO–SCCC calculation performed on the hypothetical complex. These H_{ii} values (eV) were as follows: Cu ($H_{ss} = -15.54$, $H_{pp} = -9.393$, $H_{dd} = -20.81$); O ($H_{ss} = -36.3$, $H_{pp} = -19.70$); N ($H_{ss} = -34.16$, $H_{pp} = -21.16$); N_{sp^2} ($H_{sp^2,sp^2} = -24.16$, exp = 1.725). The exact geometries used for each complex along with the coordinate system are given in Figure 1.

Results and Discussion

Characterization and Properties of Complexes. All complexes under investigation, according to their molar conductivities (Table I)[16] were 1:2 electrolytes, except the bpy complex, which behaved as an 1:1 electrolyte. The most relevant IR and reflectance spectral bands of the solid compounds along with their assignments are shown in Table II. The bands attributed to the amino groups of the coordinated polyamine ligands closely resembled those of analogous complexes differing in their counterions. These groups,

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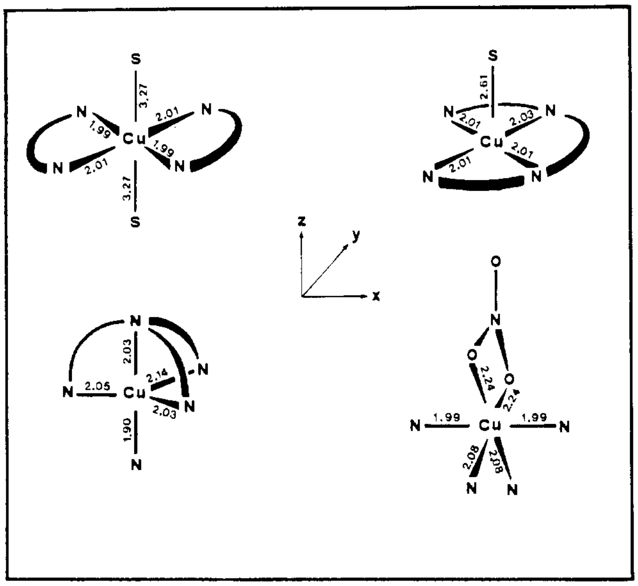

Figure 1. Structures of the complexes used for the calculations along with the coordinate system. Distances are given in Å.

along with the CH and OH ones, also gave their overtones in the near-infrared region of the spectra. Bands associated with the polyatomic anions present in the complexes were very important since they could provide information concerning their bonding mode. Thus the absorption bands shown by the perchlorate anion were typical[14,25] for ionic bonding, whereas the bands due to the nitrate group in the bpy complex excluded its ionic bonding mode. For the nitrate ligand the difference $\nu_{as} - \nu_s = 158\ \text{cm}^{-1}$ lay between those observed for the uni- and bidentate nitrate ligands,[26] and therefore an asymmetric bidentate bonding mode could be suggested for this ligand. The hexafluorophosphate anions gave two different patterns of absorption bands. Thus, for the en, trien, and tetren complexes the PF_6^- anions gave a very broad and strong band with a band half-width of 110 cm^{-1}, showing a maximum at 830–845 cm^{-1} and a shoulder at 880–890 cm^{-1}. On the other hand, for the bpy complex the same band showed only one maximum, whereas its band half-width was only 50 cm^{-1}. According to IR criteria[27] well established for the bonding mode of the PF_6^- anion, it could be inferred that in the bpy complex the PF_6^- anion was ionic, while in the en, trien, and tetren complexes at least one of the PF_6^- anions was semicoordinated. This was further supported by the appearence of a new weak band at 740 cm^{-1} in the IR spectra of the en, trien, and tetren complexes, which could be attributed to the activation of the inactive A_{1g} stretching vibration by semicoordination of the PF_6^- anion.[27] The intensity ratio of these two bands along with the absence of a clear splitting of the broad band for these complexes indicated the coexistence of a semicoordinated and an ionic PF_6^- anion.

The en complex complied with the linear function

$$[\nu(\text{Cu–N})]^2 = 7.817\nu_{\text{elec}} + 19\,600$$

suggested by Lever and Mantovani[5a] for tetragonally distorted octahedral copper(II) complexes. According to this equation the en complex showed an intermediate tetragonal distortion, which called for the presence of a semicoordinated PF_6^- anion and a water molecule in the axial positions. This is further substantiated by the inability of the water molecule to be removed by heating the complex under vacuum. The ligand field spectrum of the complex was also characteristic for tetragonally distorted octahedral copper(II) complexes[14a,28] and closely resembled that of the corresponding $Cu(en)_2(SCN)_2$ complex. Therefore, it could be presumed that the $[Cu(en)_2(OH_2)(FPF_5)](PF_6)$ complex adopts a structure similar to that found for the analogous thiocyanate complex.[21] Furthermore the room-temperature EPR ($g_\parallel = 2.177$, $g_\perp = 2.046$, $g_{av} = 2.090$) and magnetic susceptibility data ($\mu_{eff} = 1.81\ \mu_B$) closely resembled those of the thiocyanate complex.[2] The observed axial powder spectrum of the complex with $g_\parallel > g_\perp$ calls for a $|xy\rangle$ ground state (coordinate system according to the symmetry rules), as could be expected.

The ligand field spectrum of the trien complex was analogous to that of the en complex but shifted slightly to lower frequencies. This shifting could indicate either a higher tetragonal distortion or a square-pyramidal configuration. The last configuration seems to be the most probable one for the trien complex, because its ligand field spectrum closely resembled that of the corresponding square-pyramidal $[Cu(trien)(SCN)]^+$ complex.[14a,28] The trien complex gave an isotropic EPR spectrum to both room temperature and −120 °C with g_i values of 2.062 and 2.056, respectively, and a peak to peak line width of 93 G, suggesting that the barrier heights of the potential wells, determined by strong vibronic coupling along the three orthogonal axes, were small compared to the thermal energy at both temperatures.[29] The g_i value was indicative of a $|xy\rangle$ ground state with a normal room temperature μ_{eff} value of 1.87 μ_B.

The ligand field spectra of the two tetren complexes were characteristic of five-coordinate chromophores[14a,28,30] and closely resembled those of other tetren[6c] and dpt (dpt = 3,3′-diaminodipropylamine) complexes that were assigned distorted square-pyramidal structures. These structures may be viewed as intermediate between the ones of square pyramid adopted by the $[Cu(trien)(SCN)]^+$ complex and that of trigonal bipyramid adopted by the $[Cu(tren)(NCS)]^+$ complex. The shifting of the visible bands toward lower frequencies was attributed to the distortion of the square-pyramidal structure. However, the two tetren complexes showed different features in their EPR and magnetic data, which might reflect a different degree of distortion. Thus, the perchlorate complex, at room temperature, gave isotropic powder EPR spectrum with a g_i value of 2.103 and a peak to peak line width of 213 G, which at −120 °C was axial, with $g_\parallel = 2.162$ and $g_\perp = 2.021$ ($g_{av} = 2.070$). In contrast the hexafluorophosphate complex gave axial spectra with $g_\parallel = 2.397$ and $g_\perp = 2.043$ ($g_{av} = 2.167$) at room temperature and $g_\parallel = 2.390$ and $g_\perp = 2.040$ ($g_{av} = 2.160$) at −120 °C. This indicated that in the hexafluorophosphate complex the distortion is identified even at room temperature, due to its lower symmetry. On the contrary, in the less distorted perchlorate complex its distortion is identified only at low temperatures. The large anisotropy of the $g_\parallel$ and $g_\perp$ values observed for the hexafluorophosphate complex indicated a strong distortion as well. This distortion may be explained by the semicoordination of one of the PF_6^- anions as it was inferred from the IR spectra. The strong distortion of the square-pyramidal structure of the $[Cu(tetren)](PF_6)_2$ complex was also reflected on its abnormal high μ_{eff} value of 2.17 μ_B relative to the normal value of 1.82 μ_B observed for the perchlorate complex. It should be noted that such an abnormally high μ_{eff} value of 2.22 μ_B was also observed for the bpy complex, suggesting a strongly distorted cis-octahedral stereochemistry resulting from the long-bonded asymmetric bidentate nitrate ligand in this complex. Since $g_\parallel > g_\perp$, a $|xy\rangle$ ground state can be inferred for the two tetren complexes, which is consistent with their distorted square-pyramidal configurations.

The ligand field spectrum of the bpy complex was similar to that observed for the corresponding $[Cu(bpy)_2(NO_2)]^+$ complex[2b,30c] whose structure was found to be distorted cis octahedral.[24] Depending on the length of the longer Cu–O bond, this structure could be alternatively described as an intermediate between a square pyramid and a trigonal bipyramid. Such a structure was recently proposed[12] for the Cu(terpy)Br_2 complex, with spectral

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data similar to those of the nitrite and nitrate bpy complexes. The rhombic g_{ii} values, $g_3 = 2.227$, $g_2 = 2.149$, and $g_1 = 2.023$ ($g_{av} = 2.135$), of the bpy complex were consistent with a $|z^2\rangle$ ground state. Finally, the possibility of a water molecule coordinated to the bpy complex is ruled out because heating the complex under vacuum did not change its spectral data although the water molecule was easily removed.

Electronic Structure of Complexes. The calculated ground-state one-electron energies, charge distributions, and partial wave analyses for the valence molecular orbitals associated with both the central atom and ligand valence AO's of the compounds studied are summarized in Tables III–VI.[31]

The occupied valence molecular orbitals of the complexes have energies in the range −31.4 to −10.4 eV. There is an efficient mixing of metal and ligand orbitals for all complexes studied. Furthermore, where it was allowed by the symmetry rules, the metal part of the ground state could be mixed by other metal part functions of the same symmetry. In each case the SOMO (single occupied molecular orbital) corresponded to the expected ground state according to the symmetry of the complex.

The electronic ground state of the elongated tetragonally distorted octahedral (D_{2h}) $Cu(en)_2(SCN)_2$ complex is $(3b_{2g})^2(2b_{3g})^2(11a_g)^2(12a_g)^2(7b_{1g})^1 = {}^2B_{1g}$. The in-plane σ bonding of the complex results mainly from the bonding $6b_{1g}$ and the antibonding $7b_{1g}$ MO's having substantial metal and ligand character. The analysis of the charge distribution reveals that the $6b_{1g}$ and $7b_{1g}$ MO's have 35% and 54% metal d_{xy} character with the rest charge located on the b_{1g} σ LGO's of the two en ligands. The major contribution to the axial Cu–S σ bonding arises from the bonding $10a_g$ and antibonding $12a_g$ MO's, having 14% and 72% metal d_{z^2} character, respectively, and the rest charge is located on the sulfur p_z AO's. Finally, the corresponding filled d antibonding orbitals $3b_{2g}$ (d_{xz}), $2b_{3g}$ (d_{yz}), and $11a_g$ ($d_{x^2-y^2}$) have almost pure metal d character with less than 5% ligand character. These predominantly metal d orbitals contain linear combinations of d functions allowed by symmetry.

The electronic ground state of the square-pyramidal (C_{2v}) $[Cu(trien)(SCN)]^+$ complex is $(20a_1)^2(7b_1)^2(6b_2)^2(21a_1)^2(10a_2)^1 = {}^2A_2$. The σ bonding of this complex is mainly determined by seven MO's with substantial metal d and ligand σ character. The $9a_2$ and $10a_2$ MO's, having 35% and 51% metal d_{xy} character, respectively, were responsible for the σ bonding in the basal plane of the square pyramid. On the other hand, the $18a_1$ and $21a_1$ MO's, with 21% and 61% metal d_{z^2} character, respectively, contributed to the σ bonding of the central atom with the apical ligand. In addition a contribution to the σ bonding results also from the $5b_2$ (d_{yz}), $7b_1$ (d_{xz}), and $6b_2$ (d_{yz}) orbitals, which are delocalized on the whole molecule and have 31%, 69%, and 57% metal d character, respectively. Such a contribution was absent in the elongated octahedral (D_{2h}) complex. Finally, the only antibonding predominantly metal d orbital that is almost a pure $d_{x^2-y^2}$ orbital, was the $20a_1$ MO with only 6% ligand character.

In contrast to the two previous complexes, no antibonding predominantly metal d orbital with almost pure d character existed in the trigonal-bipyramidal (D_{3h}) $[Cu(tren)(NCS)]^+$ complex, whose electronic ground state is $(9e'')^2(10e'')^2(17e')^2(18e')^2(13a_1')^1 = {}^2A_1'$. Therefore, all the metal d AO's were highly mixed with the ligands σ-LGO's to form the MO's that describe the σ bonding in the complex. The major contribution to the σ bonding arises from the following nine MO's. The $17e'$ (d_{xy}) and $18e'$ ($d_{x^2-y^2}$) MO's, with 60% and 56% metal d character, respectively, contributed only to the σ bonding in the equatorial plane. In contrast, the axial σ bonding involves the $9e''$ (d_{xz}) and $10e''$ (d_{yz}) MO's, which have 79% and 80% metal d character, respectively. The last five MO's, $11a_1'$ (d_{z^2}), $7e''$ (d_{xz}), $15e'$ ($d_{x^2-y^2}$), $16e'$ (d_{xy}) and $13a_1'$ (d_{z^2}) are delocalized on the whole molecule and have 17%, 28%, 15%, 19%, and 53% metal d character, respectively.

Finally, the electronic ground state of the hypothetical cis-octahedral (C_{2v}) $[Cu(N_{sp^2})_4(NO_3)]^+$ complex is $(7a_1)^2(1a_2)^2(3b_1)^2(4b_2)^2(9a_1)^1 = {}^2A_1$. There are two antibonding predominantly metal d orbitals, namely $1a_2$ (d_{xy}) and $3b_1$ (d_{xz}) with less than 4% ligand character. The σ bonding is mainly determined by ten MO's with substantial metal and ligand character. The $3a_1$, $1b_1$, $2b_2$, and $5a_1$ MO's, possessing 23% 4s, 20% $4p_x$, 23% $4p_y$ and 29% $d_{x^2-y^2}$ metal character, respectively, contributed to the σ bonding of the four hypothetical N_{sp^2} donor atoms with the central atom. On the other hand, the $7a_1$ (d_{z^2}), $4b_2$ (d_{yz}), $8a_1$ ($d_{x^2-y^2}$) and $6b_2$ (d_{yz}) MO's were σ MO's localized on the $Cu(NO_3)$ moiety and have 72%, 49%, 38%, and 28% metal d character, respectively. Moreover, the σ antibonding $9a_1$ MO, with 58% metal d character (38% $d_{x^2-y^2}$ and 20% d_{z^2}), is delocalized on the whole molecule whereas the bonding $4a_1$ MO, with only 6% metal $4p_z$ character, seems to be a nonbonding MO localized on the two oxygen donor atoms of the nitrate group.

From the preceding molecular orbital analysis of the chemical bonding in the four Cu(II) complexes possessing regular geometries in the structural pathway, it is obvious that the major difference is in the number and nature of the metal d AO's involved in the σ bonding. These differences could provide a sound explanation for the variations of the electronic properties (EPR and electronic spectral data) observed for the copper(II) polyamine complexes present in the structural pathway.[2b] Moreover, another interesting feature to emerge from this analysis is that there was no participation of the metal 4s and 4p AO's in the σ bonding except in the case of the hypothetical $[Cu(N_{sp^2})_4(NO_3)]^+$ complex where a rather small participation of these orbitals exists. These orbitals, however, have an appreciable participation in the virtual MO's of lower energies.

In addition to the occupied levels the virtual (unoccupied) MO's of the complexes have energies in the range −13.9 to 99.4 eV. For the en, trien, and tren complexes the LUMO's ($4b_{1u}$, $11a_2$, and $11e''$) are located on the thiocyanate groups. Therefore, the nucleophilic substitution of the thiocyanate groups in these complexes may be rationalized in terms of addition of electrons to the LUMO's. For the hypothetical bpy complex the LUMO, $5b_1$, is localized in the nitrate group, which in turn will be the reactive center toward nucleophilic substitution reactions.

Table VII gives the two-center energy terms and the Mulliken overlap population for the coordination bonds together with the Mulliken net charges on the bonded atoms of the complexes under investigation. From the examination of the results shown in Table VII the following conclusions concerning the nature and strength of the coordination bonds could be drawn. For the $Cu(en)_2(SCN)_2$ complex the Cu–N bonds are stronger than the Cu–S bonds, in good agreement with the axial position of the two SCN^- groups in the elongated octahedral structure of the complex. The opposite was true for the $[Cu(trien)(SCN)]^+$ complex showing that the SCN^- group is strongly bonded in this complex in accordance with its square-pyramidal structure. In the tren complex the Cu–NCS bond is stronger than the Cu–N bonds of the tren ligand, whereas in the bpy complex the Cu–N bonds are stronger than the Cu–O bonds. Finally, an assessment of the relative strengths of the $Cu-NH_2$, Cu–NHR, and $Cu-NR_2$ bonds may be obtained:

$$Cu{-}NH_2 < Cu{-}NHR < Cu{-}NR_2$$

This trend is in accordance with the basicity of the nitrogen donor atoms in the three types of the amine groups.

Interpretation of the Electronic Spectra. Assignments (Tables VIII and IX) were made by associating the observed bands with the transitions they most nearly match in energy.

For the elongated octahedral $Cu(en)_2(SCN)_2$ complex the broad absorption band envelope in the visible region covers the four spin-allowed but symmetry-forbidden d–d transitions along with one symmetry-allowed y-polarized LMCT transition. The band maximum occurs at the region where the LMCT transition absorbs. The presence of the LMCT transition under the crystal field band envelope explains the relatively high intensity of the forbidden d–d transitions through an intensity-borrowing mechanism.[32] The band at 27.03×10^3 cm^{-1} observed for this complex

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(31) Supplementary material.

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Table VII. Two-Center Energy Terms and Overlap Population for the Coordination Bonds Along with the Net Charges of the Bonded Atoms for the (Polyamine)copper(II) Complexes

					net charge	
compd	point group	Cu-X[a]	energy, eV	overlap pop.	Q(Cu)	Q(X)
$Cu(en)_2(SCN)_2$	D_{2h}	Cu-N	-1.765	0.191	1.082	-0.415
		Cu-S	-0.825	0.083		-0.605
$[Cu(trien)(SCN)]^+$	C_{2v}	Cu-N_p	-1.655	0.184	1.131	-0.412
		Cu-N_s	-1.533	0.163		-0.420
		Cu-N_s	-1.722	0.185		-0.467
		Cu-N_p	-1.284	0.159		-0.494
		Cu-S	-3.339	0.336		-0.584
$[Cu(tren)(NCS)]^+$	D_{3h}	Cu-N_t	-2.048	0.205	1.073	-0.362
		Cu-N_p	-1.304	0.157		-0.541
		Cu-N_p	-0.729	0.101		-0.570
		Cu-N_p	-1.165	0.145		-0.519
		Cu-N	-3.602	0.315		-0.763
$[Cu(N_{sp^2})_4(NO_3)]^+$	C_{2v}	Cu-N	-6.637	0.427	0.179	0.390
		Cu-N	-5.758	0.374		0.314
		Cu-N′	-5.758	0.374		0.314
		Cu-N′	-6.637	0.427		0.390
		Cu-O	-2.621	0.134		-0.571
		Cu-O	-2.621	0.134		-0.571

[a] N_s = secondary amine group; N_p = primary amine group; N_t = tertiary amine group.

Table VIII. Electronic Absorptions and Assignments for $Cu(en)_2(SCN)_2$ and $[Cu(N_{sp^2})_4(NO_3)]^+$ Complexes

$\bar{\nu}$, $\times 10^3$ cm^{-1}			
obsd	calcd	electronic transition	gen classification
	$Cu(en)_2(SCN)_2$ (D_{2h})		
43.86[a]	50.89	$1a_u \rightarrow 7b_{1g}$	M(d) ← L(σ)
	49.73	$2a_u \rightarrow 7b_{1g}$	
	47.13	$5b_{3u} \rightarrow 7b_{1g}$	
	38.02	$3b_{2u} \rightarrow 7b_{1g}$	
	33.56	$6b_{3u} \rightarrow 7b_{1g}$	
	30.01	$7b_{3u} \rightarrow 7b_{1g}$	M(d) ← L(σ)
	25.79	$6b_{2u} \rightarrow 7b_{1g}$	
	20.98	$9b_{3u} \rightarrow 7b_{1g}$	
19.10[a]	19.09	$3b_{2g} \rightarrow 7b_{1g}$	M(d) ← M(d)
	19.03	$2b_{3g} \rightarrow 7b_{1g}$	
	18.47	$11a_g \rightarrow 7b_{1g}$	
14.50[a]	15.74	$12a_g \rightarrow 7b_{1g}$	M(d) ← M(d)
	$[Cu(N_{sp^2})_4(NO_3)]^+$ (C_{2v})		
47.17	49.71	$2b_1 \rightarrow 9a_1$	M(d) ← L(π)
	47.87	$8a_1 \rightarrow 5b_1$	L(π*) ← L(σ)
	44.69	$2a_2 \rightarrow 9a_1$	M(d) ← L(π)
39.52	42.67	$4b_1 \rightarrow 5b_1$	L(π*) ← L(π)
	41.12	$3b_2 \rightarrow 9a_1$	M(d) ← L(σ)
28.74	33.69	$6a_1 \rightarrow 9a_1$	M(d) ← L(σ)
	24.57	$7a_1 \rightarrow 9a_1$	M(d) ← M(d)
25.32	24.13	$1a_2 \rightarrow 9a_1$	M(d) ← M(d)
23.53	23.99	$3b_1 \rightarrow 9a_1$	M(d) ← M(d)
15.77	16.59	$4b_2 \rightarrow 9a_1$	M(d) ← M(d)
13.89	15.94	$8a_1 \rightarrow 9a_1$	M(d) ← L(σ)
10.71	10.74	$4b_1 \rightarrow 9a_1$	M(d) ← L(π)

[a] Values were obtained from ref 5c and 14a.

Table IX. Electronic Absorptions and Assignments for $[Cu(trien)(SCN)]^+$ and $[Cu(tren)(NCS)]^+$ Complexes

ν, $\times 10^3$ cm^{-1}			
obsd	calcd	electronic transition	gen classification
	$[Cu(trien)(SCN)]^+$ (C_{2v})		
38.31[b]	46.61	$8a_1 \rightarrow 10a_2$	M(d) ← L(σ)
	42.34	$4a_2 \rightarrow 10a_2$	
	38.83	$5a_2 \rightarrow 10a_2$	
	37.32	$6a_2 \rightarrow 10a_2$	
	33.37	$8a_2 \rightarrow 10a_2$	
	31.29	$5a_1 \rightarrow 10a_2$	
	20.05	$5b_2 \rightarrow 10a_2$	M(d) ← L(σ)
17.40[a]	17.57	$20a_1 \rightarrow 10a_2$	M(d) ← M(d)
	16.30	$7b_1 \rightarrow 10a_2$	M(d) ← M(d)
15.00[a]	15.00	$6b_2 \rightarrow 10a_2$	M(d) ← M(d)
	12.73	$21a_1 \rightarrow 10a_2$	M(d) ← M(d)
	$[Cu(tren)(NCS)]^+$ (D_{3h})		
	41.23	$9e' \rightarrow 13a_1'$	M(d) ← L(σ)
29.40[c]	32.69	$10e' \rightarrow 13a_1'$	M(d) ← L(σ)
	31.55	$11e' \rightarrow 13a_1'$	
	30.61	$12e' \rightarrow 13a_1'$	
	26.79	$13e' \rightarrow 13a_1'$	
	26.10	$14e' \rightarrow 13a_1'$	
	20.38	$15e' \rightarrow 13a_1'$	M(d) ← L(σ)
	19.86	$16e' \rightarrow 13a_1'$	
14.70[c]	15.55	$10e'' \rightarrow 13a_1'$	M(d) ← M(d)
	15.51	$9e'' \rightarrow 13a_1'$	
11.90[c]	11.09	$17e' \rightarrow 13a_1'$	M(d) ← M(d)
	9.70	$18e' \rightarrow 13a_1'$	

[a] Values were obtained from ref 28. [b] This value was obtained from the UV electronic reflectance spectrum of $[Cu(trien)](PF_6)_2$ prepared in this study. [c] Values were obtained from ref 30a.

is also assigned to LMCT transitions.

For the square-pyramidal $[Cu(trien)(SCN)]^+$ complex the absorption band envelope in the visible region covers the two symmetry-allowed x- and y-polarized $6b_2$, $7b_2 \rightarrow 10a_2$ ($^2A_2 \leftarrow {}^2B_2$) transitions, the two forbidden, $20a_1$, $21a_1 \rightarrow 10a_2$ ($^2A_2 \leftarrow {}^2A_1$) d–d transitions, and one symmetry-allowed x-polarized LMCT transition. The band maximum occurs in the region where the symmetry-allowed d–d and LMCT transitions absorb. The d–d transitions of the square-pyramidal complex are shifted to lower frequencies relative to those of the elongated octahedral complex in accordance with the ligand field strengths in these two complexes.

For the trigonal-bipyramidal $[Cu(tren)(NCS)]^+$ complex the broad absorption band envelope in the visible region covers the two symmetry-allowed x,y-polarized and the two symmetry-forbidden d–d transitions with the maximum at the low-frequencies region where the allowed transitions absorb. The band envelope is free from the symmetry-allowed x,y-polarized LMCT transitions, which absorb at 19.86 and 20.38 × 10^3 cm^{-1}.

Finally, for the hypothetical distorted cis-octahedral bpy complex, the broad absorption band envelope shows two distinct maxima of equal intensity at frequencies where the two symmetry-allowed z- and y-polarized d–d transitions absorb.

For all complexes the ultraviolet region of the spectra is dominated by a number of symmetry-allowed CT transitions. All these transitions are covered under a single band, with a maximum depending on the stereochemistry of the complexes under investigation. Generally, the trend observed is elongated octahedral > square pyramidal > trigonal bipyramidal. No pure intraligand

$\sigma \rightarrow \sigma^*$ transitions have been observed in this region of the spectra, for these transitions were predicted to occur at higher energies in the far-ultraviolet region. The intraligand transitions due to the bpy ligand were also present in the ultraviolet region of the bpy complex. These intraligand transitions, which are of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ type, have been assigned on the basis of IEMO calculations, which were carried out on the free ligand as well. All these transitions along with the intraligand transitions due to the NO_3^- ligand (Table VIII) are covered under the same band envelope, with its maxima and shoulders given in Table II.

Calculation of the EPR Parameters. The $\mathbf{g}_{ii}$ and $\mathbf{A}_{ii}$ tensors were calculated by using the conventional perturbation approach developed for Cu(II) complexes of different geometries.[2,33] Thus, for the $Cu(en)_2(SCN)_2$ complex (D_{2h} symmetry) the $\mathbf{g}_{ii}$ tensors were estimated by using the expressions given by Gersmann and Swalen[34] while for the $\mathbf{A}_{ii}$ tensors those given by Maroney et al.[36] were used. In addition the calculated g_{ii} values were further corrected by taking into account the mixing of the $|x^2 - y^2\rangle$ and $|z^2\rangle$ states according to the functions given by Waite and Hitchman.[35] Finally, the known expressions given by Maroney et al.[36] were also used for the estimation of the $\mathbf{g}_{ii}$ tensors of the complex. It should be noted that although these equations do not take into account overlap integrals yielded g_{ii} values ($g_{xx} = 2.038$, $g_{yy} = 2.039$, and $g_{zz} = 2.222$) in close agreement with the experimental ones. For the square-pyramidal $[Cu(trien)(SCN)]^+$ complex of C_{2v} symmetry, the $\mathbf{g}_{ii}$ tensors were calculated by using the expressions[36]

$$g_{zz} = g_{\parallel} = 2.0023 - 8\lambda\alpha^2 \sum_{n=1}^{n} \frac{\beta_n^2}{\Delta n}$$

$$g_{xx,yy} = 2.0023 - 2\lambda\alpha^2 \sum_{x=1}^{x} \frac{\delta_x^2}{\Delta_x}$$

where all symbols have the meanings defined in Table X. The $\mathbf{A}_{ii}$ tensors for this complex were calculated by using the expressions given by Gatteschi et al.,[37] taking also into account the deviation of the geometry from the ideal square-pyramidal stereochemistry. The same expressions for the $\mathbf{A}_{ii}$ tensors along with the expressions for the $\mathbf{g}_{ii}$ tensors given in this paper[37] have been also used for the calculation of the magnetic parameters for the trigonal-bipyramidal $[Cu(tren)(NCS)]^+$ complex of D_{3h} symmetry. Finally, for the cis-octahedral bpy complex, any calculation of the magnetic parameters would be meaningless since the EHMO calculations were carried out on a hypothetical complex and not on the real one.

The eigenvectors of the antibonding MO's along with the calculated $\mathbf{g}_{ii}$ and $\mathbf{A}_{ii}$ tensors for the three complexes are given in Table X. Generally, there is a good agreement between calculated and experimental values of the magnetic parameters, especially when the overlap integrals are not neglected. Thus, for the D_{2h} complex the experimental values of the $\mathbf{g}_{ii}$ tensors obtained[38] from the single-crystal EPR data are $g_{xx} = 2.053$, $g_{yy} = 2.036$, and $g_{zz} = 2.199$, very close to those calculated. Unfortunately, no experimental values for the $\mathbf{A}_{ii}$ tensors of the D_{2h} complex exist for comparison. For the square-pyramidal complex the experimental g_{ii} values[39] are 2.050, 2.040, and 2.204 for g_{xx}, g_{yy}, and g_{zz}, respectively. The A_{ii} values of the complex are found in the range of the values observed[37] for copper(II) complexes with stereochemistries intermediate between the two ideal structures of the square pyramid and trigonal bipyramid (20 to 60 for A_{xx}, −70 to 15 for A_{yy}, and −130 to −70 for A_{zz}).[40] These values are consistent with the distorted square-pyramidal structure of the complex. Analogous is also the situation for the trigonal-bipyramidal complex, for which the experimental g_{ii} values[2] are $g_{xx} = 2.083$, $g_{yy} = 2.132$, and $g_{zz} = 2.157$. For this complex the A_{ii} values are also in accordance with the distorted trigonal-bipyramidal structure of the complex. In spite of neglecting all overlap integrals for the last two complexes, the agreement between calculated and experimental values of the $\mathbf{g}_{ii}$ tensors is good. Thus, we can conclude that the EHMO method gives a very good MO treatment of the magnetic parameters for copper(II) complexes, which could help to rationalize some general features of the EPR spectra.

Table X. Eigenvectors of the Antibonding Molecular Orbitals Along with the Calculated Values of EPR Parameters for (Polyamine)copper(II) Complexes

orbital	Cu(II) d AO	eigenvectors symbol[a]	eigenvectors value	EPR params
		$Cu(en)_2(SCN)_2$ (D_{2h})		
$7b_{1g}$[b]	xy	α	−0.8067	$g_{xx} = 2.056$
$12a_g$	z^2		0.8168	$g_{yy} = 2.034$
	$x^2 - y^2$		−0.148	$g_{zz} = 2.180$
$11a_g$	$x^2 - y^2$	β	−0.9704	$A_{xx} = -43.82$[c]
	z^2		−0.1554	$A_{yy} = -44.11$
$2b_{3g}$	yz	δ_2	0.795	$A_{zz} = -149.93$
$3b_{2g}$	xz	δ_1	0.7911	
$2b_{2g}$	xz	δ_3	0.1199	
$1b_{3g}$	yz	δ_4	−0.0701	
		$[Cu(trien)(SCN)]^+$ (C_{2v})[d]		
$10a_2$	xy	α	0.7831	$g_{xx} = 2.031$
$6b_2$	yz	δ_1	−0.638	$g_{yy} = 2.050$
$7b_1$	xz	δ_2	−0.6131	$g_{zz} = 2.171$
$20a_1$	$x^2 - y^2$	β_1	0.847	$A_{xx} = 45.73$
$21a_1$	z^2		−0.7678	$A_{yy} = -28.40$
$5b_2$	yz	δ_3	−0.5042	$A_{zz} = -91.00$
$6b_1$	xz	δ_4	0.3106	
$4b_2$	yz	δ_5	−0.3746	
$17a_1$	$x^2 - y^2$	β_2	−0.1361	
$3b_2$	yz	δ_6	0.1065	
$5b_1$	xz	δ_7	−0.0903	
		$[Cu(tren)(NCS)]^+$ (D_{3h})[d]		
$13a_1'$	z^2		−0.7308	$g_{xx} = 2.0023$
$18e'$	$x^2 - y^2$		−0.7350	$g_{yy} = 2.130$
$17e'$	xy		0.7108	$g_{zz} = 2.123$
$10e''$	yz		0.7624	$A_{xx} = 59.31$
$9e''$	xz		0.8646	$A_{yy} = -50.00$
				$A_{zz} = -81.28$

[a] The symbols listed are those defined in ref 36. The appropriate symbols for the eigenvectors used in the equations given in ref 2, 34, 35, and 37 can easily be derived from the table. [b] Our estimated values for the overlap integral and the α' eigenvector for the b_{1g} LGO were −0.1208 and 0.276, respectively. [c] All A_{ii} values are in units of 10^{-4} cm^{-1}. [d] The deformation parameter β for these complexes were taken as −12 and −30, respectively.[37]

Registry No. $[Cu(en)_2(OH_2)(FPF_5)](PF_6)$, 97783-84-1; $[Cu(trien)(FPF_5)](PF_6)$, 97783-86-3; $[Cu(tetren)(FPF_5)](PF_6)$, 97783-88-5; $[Cu(tetren)](ClO_4)_2$, 33292-80-7; $[Cu(bpy)_2(NO)_3](PF_6)$, 97783-89-6.

Supplementary Material Available: Table I (analytical data and some physical properties) and Tables III–VI (valence molecular orbitals of the complexes) (5 pages). Ordering information is given on any current masthead page.

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