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EXAFS Study and Magnetic Properties of Copper(II) Chloranilato and Bromanilato Chains: A New Example of Orbital Reversal

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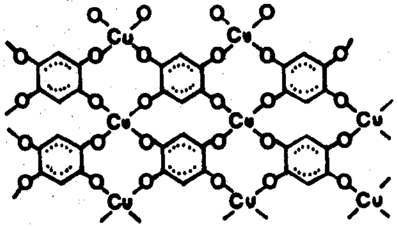
The compounds $Cu(C_6O_4X_2)$ and $Cu(C_6O_4X_2)L_2$ where $(C_6O_4X_2)^{2-}$ is the chloranilato (X = Cl) or the bromanilato (X = Br) ion and L a nitrogen-containing ligand such as ammonia, pyridine, imidazole, benzimidazole, 2-methylimidazole, or aniline have been synthetized and their structures determined by the extended X-ray absorption fine structure (EXAFS) technique. $Cu(C_6O_4Br_2)$ is particularly appropriate for EXAFS work, since it permits the investigation of X-ray absorption spectra on the high-energy side for both copper and bromine *K* edges. The EXAFS spectra very strongly support the planar ribbon structure; they are incompatible with a layer structure. Fixing two L ligands per metallic center brings about modifications of EXAFS spectra which are consistent with a rhombic distortion of the copper sites, with two short Cu–N distances, two short Cu–O distances, and two long Cu–O distances. The magnetic properties of all the prepared compounds have been studied in the 3.8–300 K temperature range (1.2–300 K for $Cu(C_6O_4Cl_2)(NH_3)_2$). The magnetic data are consistent with a chain structure, the intrachain exchange parameter J ($\mathcal{H} = -J\sum_{i=0}^{N-1}\hat{S}_i\cdot\hat{S}_{i+1}$) being −24.5 and −22.3 cm^{-1} for $Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Br_2)$, respectively, and between −1.5 and −3.8 cm^{-1} for the $Cu(C_6O_4X_2)L_2$ compounds. An orbital interpretation of the coupling is proposed. The drastic decrease of the coupling when two L ligands are fixed per metallic center is interpreted as resulting from a reversal of the magnetic orbitals due to the rhombic distortion of the copper sites.

Introduction

Today it is well-known that a good knowledge of the structure is needed to allow a thorough interpretation of the magnetic properties of polynuclear complexes with paramagnetic centers. The study of the relations between structure and magnetic properties is an active field in inorganic chemistry. The polymeric complexes present some specific problems. In scarce cases, single crystals can be obtained. This allows a structural investigation by standard radiocrystallography. But frequently, these compounds are prepared as polycrystalline powders which are not suitable for X-ray structural study. The example of copper oxalate $CuC_2O_4\cdot{}^1/_3H_2O$ is particularly striking in this respect.[3] All the attempts to grow single crystals have been unsuccessful. Therefore the interpretation of the observed magnetic behavior has been impossible, up to very recently.[4] When all efforts to grow single crystal of a polymeric compound suitable for X-ray study have failed, other methods must be used. The first method consists of determining the structure from vibrational spectroscopy data. Such an approach will give information on the way the atoms are bound. But, in no case, will it give information on the values of the distances between metallic centers and bridging atoms. The second method consists of deducing the structure of a $(M–X)_n$ chain from the actual structure of a binuclear complex with the same M–X–M bridging system. That has been done recently for the copper rubeanates $CuC_2S_2N_2R_2$.[5] The third method is the extended X-ray absorption fine structure (EXAFS) technique. The possibilities of the EXAFS method are being explored in several synchrotron centers, particularly in LURE[1] of the University Paris Sud. We used it to determine the structure of copper(II) oxalate.[3]

In this work, we studied the structures of (chloranilato)- and (bromanilato)copper(II), $Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Br_2)$, respectively, and of $Cu(C_6O_4X_2)(NH_3)_2$ with X = Cl and Br by using the EXAFS technique. We also synthesized $Cu(C_6O_4Cl_2)L_2$ with L = pyridine (py), imidazole (im), aniline (anil), benzimidazole (bzim), and 2-methylimidazole (2-Meim). Then, we investigated the magnetic properties of these compounds and tried to interpret them in correlation with the structural data. This paper has two aims: (i) to test the efficiency of the EXAFS technique in the study of polynuclear complexes (we largely focused on $Cu(C_6O_4Br_2)$; indeed, this compound allowed us to study the X-ray absorption spectra on the high-energy side for both copper and bromine X-ray absorption edges); (ii) to pursue a thorough study of the mechanism of the exchange interaction.[4-6]

The first structural and magnetic studies of $Cu(C_6O_4X_2)$ compounds appeared in 1960.[7] The authors noticed that two structures were possible with X = H: either a layer structure or a ribbon structure as shown in **1** and **2**, respectively.



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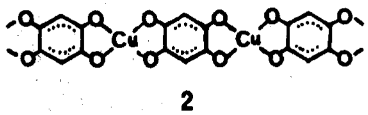

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In 1963, the authors claimed that they had been able to grow a single crystal of $Cu(C_6O_4Cl_2)$, and they gave the lattice parameters corresponding to a triclinic unit cell.[8] However, the structure has never been published. In a subsequent paper, they studied the magnetic properties of these compounds and

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interpreted them as a ribbon structure[9] compatible with the X-ray powder spectrum. They proposed two alternative values for the exchange parameter in $Cu(C_6O_4H_2)$, one calculated by using an Ising Hamiltonian ($J = -33.3$ cm^{-1}) and the other by using a Heisenberg Hamiltonian ($J = -19.5$ cm^{-1}). It appeared to us that the structure–magnetic property relation for these compounds deserved to be reinvestigated. In addition, the compounds $Cu(C_6O_4X_2)L_2$ where L is a nitrogen-containing ligand apparently have never been prepared. The comparison of their magnetic properties with those of the compounds without the L ligand allowed us to find a new example[4] of orbital reversal in copper(II) linear chains resulting from the distortion of the copper sites when two L ligands are fixed on each metallic center.

Experimental Section

Syntheses. $Cu(C_6O_4Cl_2)$ is prepared by pouring dropwise a solution of 1 mmol of chloranilic acid in 100 cm^3 of ethanol into a solution of 1 mmol of $CuCl_2 \cdot 2H_2O$ in 20 cm^3 of ethanol. The green precipitate is filtered, washed with ethanol, and dried under vacuum. $Cu(C_6O_4Br_2)$ is obtained in a similar way. A typical preparation of $Cu(C_6O_4Cl_2)L_2$, L = ammonia, pyridine, imidazole, aniline, 2-methylimidazole, or benzimidazole, is as follows. One millimole of chloranilic acid in 50 cm^3 of water is added dropwise to a solution of 1 mmol of $CuCl_2 \cdot 2H_2O$ and 4 mmol of the L base in 50 cm^3 of water. The precipitate is washed with water and ethanol and dried under vacuum. $Cu(C_6O_4Br_2)(NH_3)_2$ is obtained in a manner similar to that for $Cu(C_6O_4Cl_2)(NH_3)_2$. All the complexes $Cu(C_6O_4X_2)$ and $Cu(C_6O_4X_2)L_2$ have perfectly resolved X-ray powder spectra. All the attempts to grow single crystals were unsuccessful. The chemical analyses were performed for all the elements but oxygen and gave quite satisfactory results. Typical analyses follow. Anal. Calcd for $Cu(C_6O_4Br_2)$: Cu, 17.68; C, 20.05, Br, 44.46. Found: Cu, 17.7; C, 19.66; Br, 43.79. Calcd for $Cu(C_6O_4Cl_2)(NH_3)_2$: Cu, 20.86; C, 23.69; H, 1.98; Cl, 23.28; N, 9.20. Found: Cu, 21.4; C, 23.39; H, 2.14; Cl, 23.45; N, 8.90. Calcd for $Cu(C_6O_4Cl_2)(py)_2$: Cu, 14.8; C, 44.82; H, 2.35; Cl, 16.5; N, 6.53. Found: Cu, 15.5; C, 44.49; H, 2.47; Cl, 16.30; N, 6.23.

EXAFS Structural Study. The EXAFS technique, its theory, and its possibilities have been abundantly described elsewhere.[10–14] The key steps of the EXAFS spectra analysis are Fourier transformation from *k* to *R* space, Fourier filtering, and least-squares fitting of the *k*-space to the theoretical curves:

$$k[\chi(k)] = \sum_i \frac{A_i e^{-2\sigma_i^2 k^2 - 2R_i/\lambda_i}}{R_i^2} [f_i(k)] \sin [2kR_i + \phi_i(k)]$$

where nonlinearly fitted parameters are $2\sigma_i^2$, R_i, and E_0. $k = [(2me/h^2)(h\nu - E_0)]^{1/2}$ is the wave vector of the photoelectron ejected from the absorbing atom with an energy $(h\nu - E_0)$ above the *K* edge of the element, $\chi(k) = (\mu - \mu_0)/\mu$ is the normalized oscillatory component of the absorption coefficient, A_i is a linear scaling coefficient, proportional to the number of atoms in the *i*th shell, $2\sigma_i^2$ is a damping coefficient related to thermal and static disorder, λ_i is the mean free path of the electron, R_i is the absorbing atom–neighbor distance for the *i*th shell, and $f_i(k)$ and $\phi_i(k)$ are the amplitude and phase shift functions characteristic of the *i*th shell taken from Teo and Lee.[14] The quality of the fit is determined by a weighted agreement factor $\rho = \sum W_t(\chi_{\mathrm{exptl}} - \chi_{\mathrm{calcd}})^2 / \sum W_t \chi_{\mathrm{exptl}}^2$. Here the weighting factor W_t is zero in the range 1.6–3 Å^{-1} and equal to k^3 above 3 Å^{-1}. All the EXAFS spectra were recorded at room temperature on the EXAFS spectrometer described by Fontaine et al.[15]

Magnetic Measurements. These were carried out on polycrystalline samples of about 10 mg with a previously described Faraday type magnetometer.[4–6] Magnetic inductions of about 10 kG were used for all the samples. Independence of the magnetic susceptibility from the magnetic induction was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for diamagnetism were calculated from Pascal's table. The TIP was assumed to be 60×10^{-6} cm^3 mol^{-1} for all the compounds. In addition, for $Cu(C_6O_4Cl_2)(NH_3)_2$ the magnetic susceptibility was measured in the temperature range 1.2–4.2 K with a mutual-inductance alternative bridge used at low frequency ($\nu < 100$ Hz) described elsewhere.[16] Independence of the susceptibility from the magnetic induction, up to 2 kG, was checked at 1.2 K.

Table I. Two-Shell Fitting Results for the 0–2.8 Å Filtered Spectra, the Absorbing Atom Being Copper[a]

	E_0/eV	R/Å	$2\sigma^2$/Å^2	ρ/%
$Cu(C_2O_4) \cdot {}^1/_3H_2O$				
Cu–O	9002.79	1.97	0.019	0.57
Cu–C	8992.53	2.64	0.027	
$Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$				
fitted as: Cu–O	8994.80	1.98	0.026	0.97
Cu–C	9001.17	2.71	0.046	
$Cu(C_6O_4Cl_2)$				
Cu–O	9002.29	1.95	0.017	0.36
Cu–C	8992.23	2.71	0.010	
$Cu(C_6O_4Cl_2)(NH_3)_2$				
fitted as: Cu–O	8995.25	1.97	0.020	0.68
Cu–C	8999.41	2.65	0.029	
$Cu(C_6O_4Br_2)$				
Cu–O	9002.81	1.95	0.011	1.5
Cu–C	8990.43	2.67	0.010	
$Cu(C_6O_4Br_2)(NH_3)_2$				
fitted as: Cu–O	8993.55	1.98	0.021	1.48
Cu–C	9000.83	2.65	0.048	

[a] In the fitting procedure, we carefully checked that the fitted values of E_0 were reasonably close to the energies of the maxima of the EXAFS spectra.

Table II. Fitting Results for Shells Involving Bromine Atoms[a]

	E_0/eV	R/Å	$2\sigma^2$/Å^2	ρ/%
$\mathrm{Cu(C_6O_4}\mathit{Br}_2)$				
Br–C2	13483.2	1.86	0.011	6.7
Br–(C1 + O1)	13477.5	2.84	0.012	1.3
		3.11	0.021	
Br–Cu	13476.2	4.99	0.017	2
Br–Br	13475.3	6.55	0.010	12.5
$\mathrm{Cu(C_6O_4}\mathit{Br}_2\mathrm{)(NH_3)_2}$				
Br–C2	13484.12	1.87	0.012	8.5
Br–(C1 + O1 + O2)	13477.42	2.84	0.009	0.59
		3.14	0.025	
		3.17	0.018	
$\mathit{Cu}\mathrm{(C_6O_4Br_2)}$				
Cu–Br	8984.25	5.04	0.015	4

[a] The absorbing atom is italic.

Results and Interpretation of the EXAFS Study

Figures 1 and 2 give the experimental EXAFS spectra $k[\chi(k)]$ (*k* space) and the modulus of the Fourier transform of $k^3[\chi(k)]$ (*R* space), respectively.[30] In Tables I and II are summarized the fitting results, with the fitted edge E_0, the absorbing atom–neighbor distance *R*, the damping coefficient $2\sigma^2$, and the agreement factor ρ. Table I is concerned with the copper surrounding in a sphere of radius $R < 3$ Å corresponding to the first two peaks in the *R*-space spectra, with the *R* filtering limits 0.5–2.8 Å. It is associated with Figure 3, where the two-shell fitting spectra are presented.[30] The two-shell fitting spectra for the ammonia derivatives must be regarded only as a semiquantitative approach since the complete description of the structures would need at least five independent shells (one Cu–N, two Cu–O, and two Cu–C distances) and thus a prohibitive number of fitting parameters.

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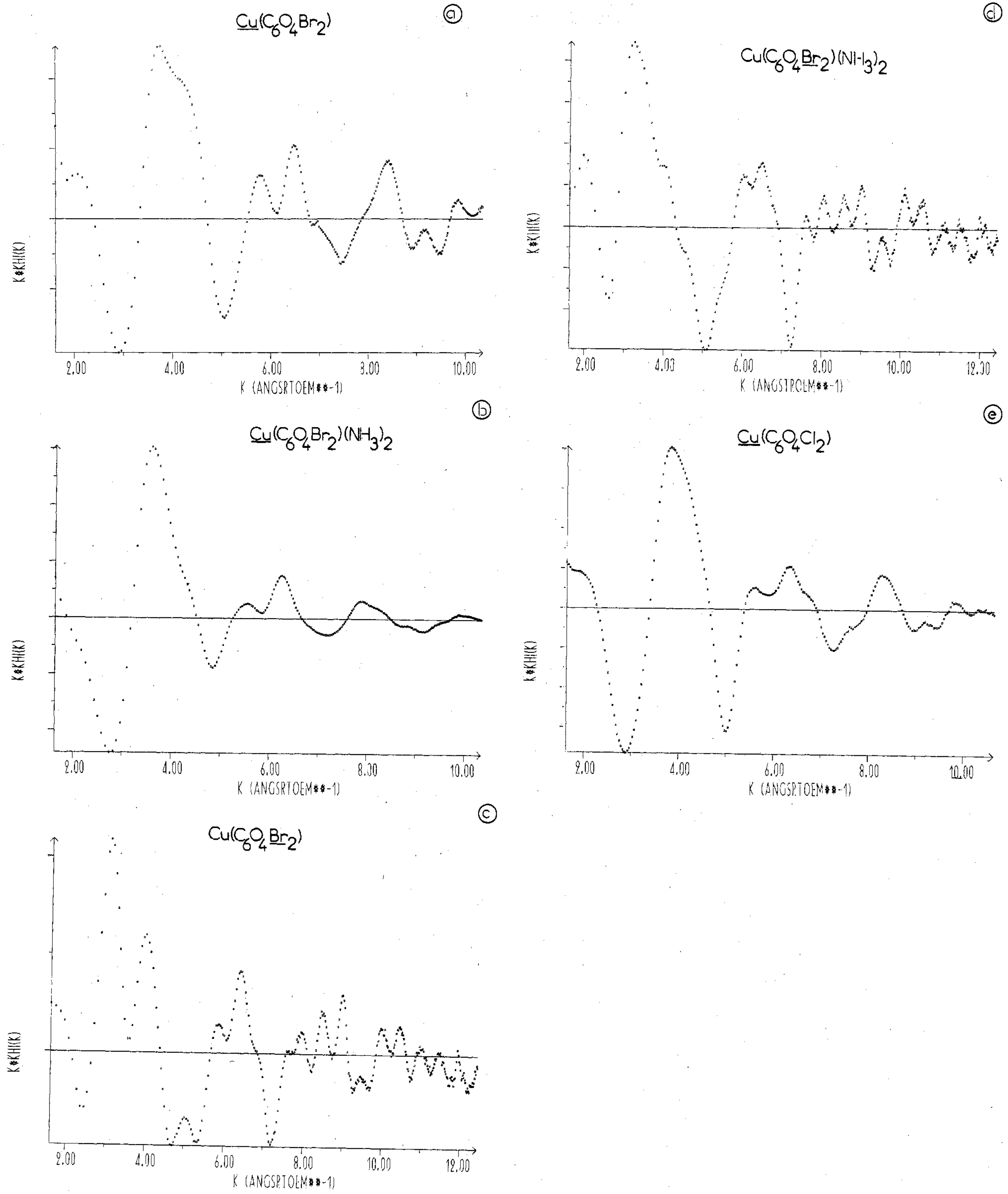

Figure 1. k-Space spectra $k[\chi(k)]$ in arbitrary units vs. k in Å^{-1} for the mentioned compounds. The absorbing atom is underlined.

Table II deals with the bromine atom in $Cu(C_6O_4Br_2)$ and $Cu(C_6O_4Br_2)(NH_3)_2$ either as a copper neighbor or as the absorbing atom.[30]

From the results of Tables I and II, we propose to discuss the two following questions: (i) Does the EXAFS study confirm the ribbon structure for $Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Br_2)$? (ii) How is the basic structure modified by fixing two nitrogen-containing ligands on each copper atom?

To answer the first question, let us consider the results of Tables I and II concerning $Cu(C_6O_4Br_2)$. The three unambiguously determined distances are Cu–O = 1.95 ± 0.02 Å, Cu–C = 2.67 ± 0.04 Å, and Br–C = 1.86 ± 0.02 Å. For the last distance, the fit is not excellent ($\rho = 0.067$). This probably comes from the used amplitude and phase shift tables.[14] However, this Br–C distance is in good agreement with published data for bromo aromatic compounds; for instance, the Br–C distance in bromobenzene is also 1.86 Å. If we assign peak 4 of Figure 2a and 4 of Figure 2c to a Cu–Br distance, we obtain *Cu*–Br = 5.04 Å and *Br*–Cu = 4.99 Å. Since O1 is nearly aligned with Cu and Br, these results may be affected

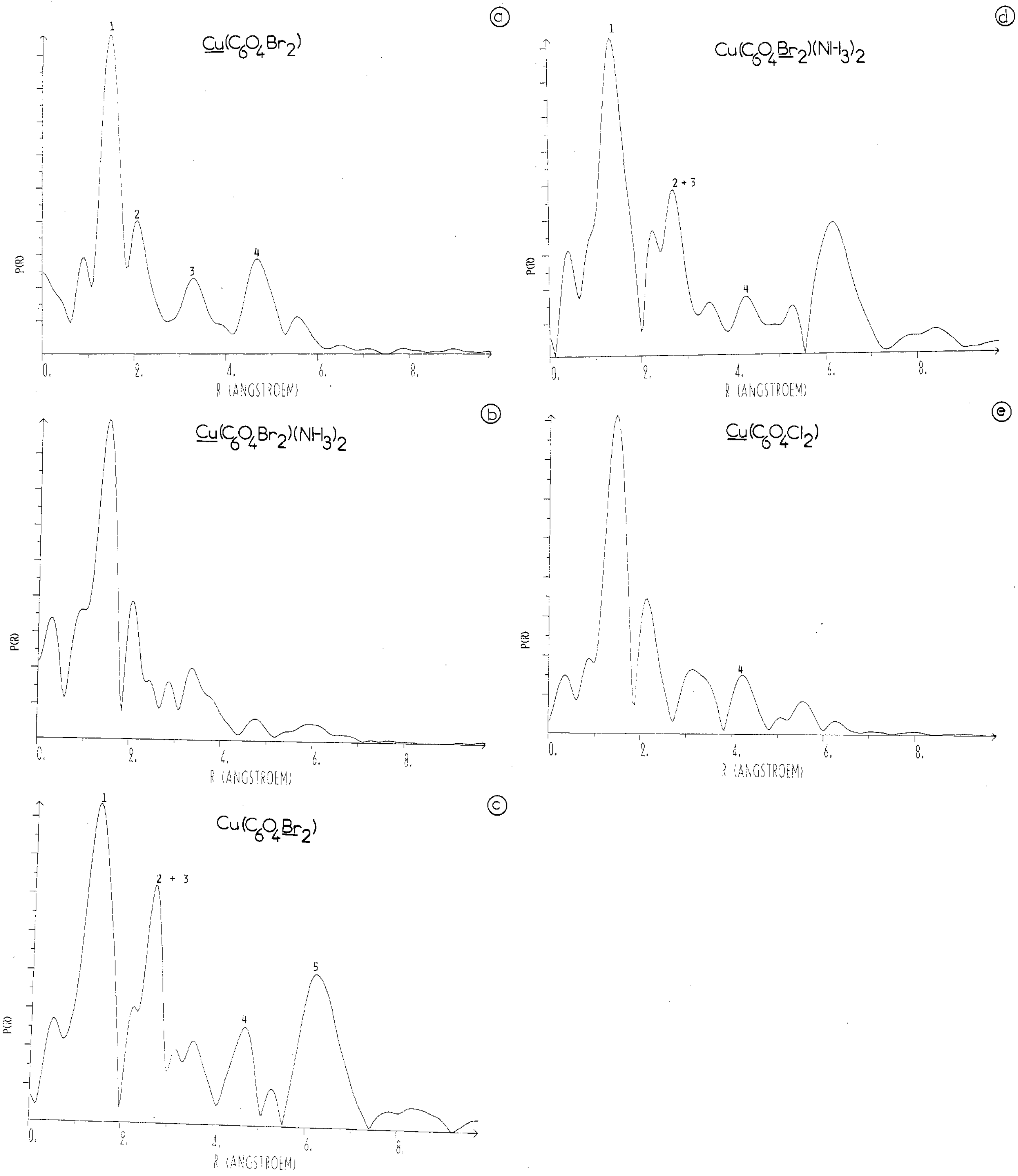

Figure 2. *R*-Space spectra FT [$k^3[\chi(k)]$] in arbitrary units vs. *R* in Å deduced from the experimental data of Figure 1.

by the multiple-scattering effect. The systematic error introduced by ignoring this effect was estimated at 0.05–0.1 Å, the obtained distances being shorter than the actual ones.[17,22] Here, the actual Cu-Br distance may be expected around 5.06 Å.

The $2\sigma^2$ values for Cu–O and Cu–C shells indicate that the four Cu–O distances are equal within 0.02 Å and that the Cu–C distances are equal within 0.04 Å. An EXAFS study cannot determine completely the molecular structure. However, the knowledge of the chloranilato compounds[18,20] helps us to determine bromanilato ion structure. We replaced chlorine atoms by bromine atoms with Cu–Br = 1.86 Å. We averaged distances and angles and found the structure **3**. If we assume a planar structure for Cu($C_6O_4Br_2$), we can compute all the copper– and bromine–neighbor distances, by fixing

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(17) A.M evaluated the magnitude of this systematic error in some compounds. For instance, in $K_3Co(CN)_6$, the uncorrected EXAFS value of the Co–N distance is 2.99 Å whereas the actual value is 3.04 Å.

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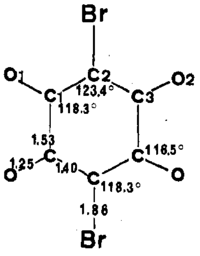

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Cu–O1 and Br–C2 (see **3** and Table III). The simulated *R*-space spectrum is shown as supplementary material.[30] The distances fitted by EXAFS methods and those computed from simple geometry calculations are quite similar. The discrepancy is less than 0.04 Å, but for Br–O and Br–Cu.

The most surprising result is the similarity of the Br–Br distances (determined by the EXAFS technique 6.55 Å; computed from the geometry model 6.58 Å). The corresponding *R*-space spectra peak (Figure 2c, peak 5) is very high compared to peaks 1, 2 + 3, and 4. This is due to the multiple scattering of the photoelectron resulting from the collinearity Br–C···C–Br. It has been shown that collinearity leads to an enhancement of the second-shell amplitude, in addition to the phase shift effect discussed above.[21,22]

At this stage, we may assert that a planar ribbon structure for $Cu(C_6O_4Br_2)$ is quite compatible with the EXAFS spectra. It remains now to show that the other hypotheses may be ruled out: (i) From the assignment of the Cu–Br peaks and the values Cu–O1 = 1.95 ± 0.02 Å, Cu–C1 = 2.67 ± 0.04 Å, and Cu–Br $\simeq$5.06 Å, it is easy to prove that the copper cannot lie out of the bromanilato planes; hence a bent ribbon structure is impossible. (ii) A planar layer structure is imcompatible with the determined Cu–O and Cu–C distances. Moreover, in such a structure, the halogen atoms would be too close to each other. (iii) An assignment of peak 4 of Figure 2a,c to a copper–copper distance in a nonplanar layer structure is also impossible. Indeed, in this case, the Cu–Br peak would be peak 3. Neither the relative amplitude of peaks 3 and 4 nor the corresponding Cu–Br distance is compatible with a layer structure. The cornerstone of our demonstration is the assignment of the Cu–Br peaks. In addition to those already given, two new arguments may be proposed to prove that peak 4 of the *R*-space spectra for $Cu(C_6O_4Br_2)$ is actually representative of the Cu–Br neighboring: (i) This peak cannot be assigned to an intermolecular interaction, for instance a Cu–Cu distance between two adjacent ribbons, since it has been shown that at room temperature the corresponding EXAFS contributions are absent,[23] owing to an intense increase of the damping coefficients $2\sigma^2$. (ii) Comparing the *k*-space spectra of $Cu(C_6O_4Br_2)$ (Figure 1a) and $Cu(C_6O_4Cl_2)$ (Figure 1e), one sees that the former has a more intense high-frequency component than the latter. This is confirmed in the *R*-space spectra (Figure 2a,e) where the most important modification due to the replacement of Cl by Br is the shift and the enhancement of peak 4. In conclusion, *our EXAFS work very strongly supports the planar ribbon structure shown in Figure 4 for* $Cu(C_6O_4Br_2)$ *and, by analogy, a similar structure for* $Cu(C_6O_4Cl_2)$. The very unlikely distorted ribbon structure corresponding to a tetrahedral environment of copper cannot be however rigorously ruled out.[31]

The fixation of two ammonia molecules per copper atom in $Cu(C_2O_4)$ and in $Cu(C_6O_4Br_2)$ has the following effects on the EXAFS spectra: (i) In the *k*-space spectra, the positions of the maxima and of the minima are somewhat shifted and the amplitude for $k \geq 5$ Å^{-1} is reduced (see Figure 1b). (ii) In the *R*-space spectra, an important reduction of the copper–halogen peaks, visible also on the bromine-edge spectra,

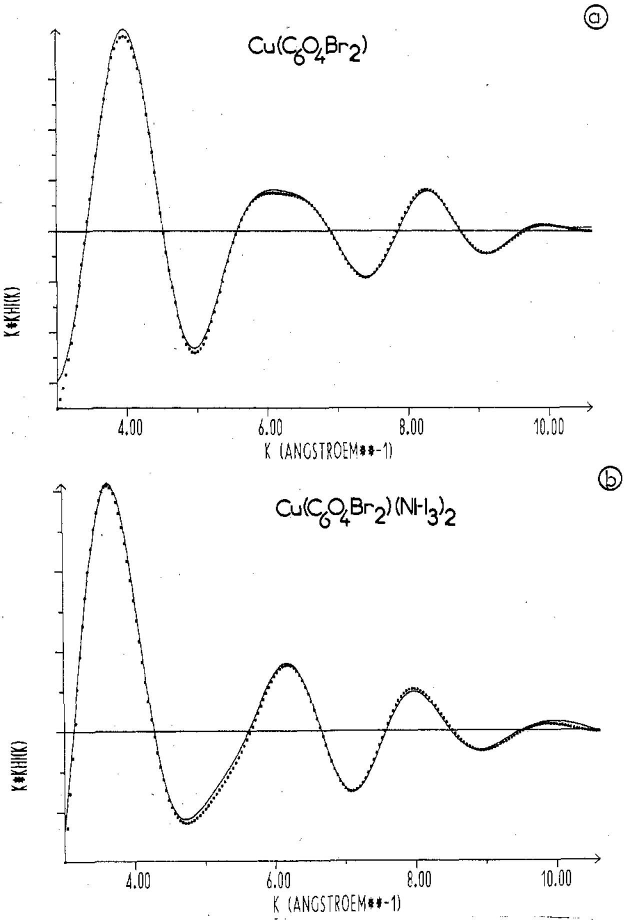

Figure 3. *k*-Space filtered spectra (points) and two-shell fittings (curve) for copper coordination spheres including all the atoms within 3 Å.

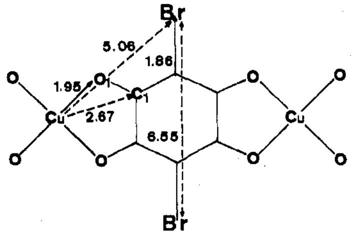

Figure 4. Structure of $Cu(C_6O_4Br_2)$ as determined by the EXAFS study (see text).

Table III. Copper Neighbor and Bromine Neighbor Distances (Å) in $Cu(C_6O_4Br_2)$ and $Cu(C_6O_4Br_2)(NH_3)_2$ Obtained by Geometry[a]

	Cu–O1	Cu–C1	Cu–C2	Cu–C3	Cu–Br	Cu–O1′
$Cu(C_6O_4Br_2)$	1.95[b]	2.65	4.03	5.07	4.98	6.26
$Cu(C_6O_4Br_2)(NH_3)_2$	1.95[b]	2.75	4.11	5.20	4.98	6.36
	2.19[b]	2.85	4.24	5.25	5.20	6.44

	Br–C2	Br–C1	Br–O1	Br–Br
$Cu(C_6O_4Br_2$	1.86[b]	2.80	3.03	6.58
$Cu(C_6O_4Br_2)(NH_3)_2$	1.86[b]	2.80	3.08	
		2.83	3.13	

[a] Bond lengths and angles of the bromanilato ion in $Cu(C_6O_4Br_2)$ are averaged from ref 20. The geometry of the bromanilato ion in $Cu(C_6O_4Br_2)(NH_3)_2$ is taken from ref 18 (see text).
[b] Fixed distances.

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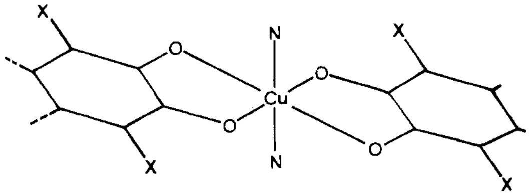
is observed (see Figure 2b,d). (iii) In the filtered *k*-space spectra corresponding to Cu–O, Cu–N, and Cu–C shells, the oscillation curves between 5 and 7 Å^{-1} are modified (see Figure 3). The corresponding fitting results are characterized by an increase of the damping coefficient $2\sigma^2$ (see Table II). Similar effects are observed for oxalato, chloranilato, and bromanilato compounds.[30] (iv) in the *R*-space spectrum of $Cu(C_6O_4Br_2)(NH_3)_2$ peaks 2 + 3 and 4 are reduced with regard to $Cu(C_6O_4Br_2)$ (see Figure 2c,d). Peak 4 is related to Cu–Br and peaks 2 + 3 are related to a mixing of Br–O1 and Br–C1. The filtered *k*-space spectra corresponding to peaks 2 + 3 may be fitted as two shells (Br–(C1 + O1)) in $Cu(C_6O_4Br_2)$ and as three shells (Br–(C1 + O1 + O2)) with Δ(Br–O) = 0.03 Å in $Cu(C_6O_4Br_2)(NH_3)_2$ (see Table II and supplementary material[30]). All these observations are consistent with the following interpretation: the trans fixation of two ammonia molecules induces a distortion of the CuO_4 site and leads to a copper surrounding with two short Cu–N bonds, two short Cu–O bonds, and two long Cu–O bonds. This situation was already observed in $Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$[24] and seems to be rather general in CuN_2O_4 chromophores.[19] The same kind of distortion of the CuO_4 site occurs in $[Cu_2(Me_5dien)_2(C_6O_4Cl_2)]^{2+}$, where the short and long Cu–O distances are 1.956 and 2.196 Å, respectively.[18] The situation observed for the bridging ligand in $[Cu_2(Me_5dien)_2(C_6O_4Cl_2)]^{2+}$ could be a realistic model for our $Cu(C_6O_4X_2)L_2$ compounds. *The fixation of ammonia on $Cu(C_6O_4Br_2)$ and $Cu(C_6O_4Cl_2)$ affects the first coordination shells of copper in the same way as it does on $Cu(C_2O_4)$.* This strongly supports the structure drawn in **4**. The very unlikely cis coordination of the ammonia molecules however cannot be rigorously ruled out. For the bromine neighborhood, the Br–C1, Br–C3, Br–O1, and Br–O2 distances are also affected by the fixation of ammonia. This suggests a distortion of the bromine site, likely due to a slight modification of C1–O1 and C3–O2 bond lengths and of O1–C1–C2 and O2–C3–C2 angles (see **3**).



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Magnetic Properties and Interpretation

The structural study via the EXAFS technique showed that the $Cu(C_6O_4X_2)$ and $Cu(C_6O_4X_2)L_2$ compounds most probably had a chain-ribbon structure. Thus the measured magnetic susceptibility χ_M may be expressed according to $\chi_M = \chi_C(1 - \rho) + \chi_I\rho + N\alpha$ by taking into account a weak proportion ρ of paramagnetic impurity including ends of chain. χ_C is the intrinsic susceptibility of the chain, χ_I the susceptibility of the impurity, and $N\alpha$ the TIP. An analytical expression for χ_C dependent on the J exchange parameter of the phenomenological Heisenberg Hamiltonian $-J\sum_{i=0}^{N-1}\hat{S}_i\hat{S}_{i+1}$ and on the g factor was proposed by Estes et al.[25] χ_I was assumed to follow the Curie law $\chi_I = N\beta^2g^2/4kT$. The J, g, and ρ parameters were determined by least-squares fitting in order to minimize the R agreement factor defined as $\sum(\chi_M^{\text{obsd}} - \chi_M^{\text{calcd}})^2/\sum(\chi_M^{\text{obsd}})^2$. The values of J, ρ, and R for all the studied compounds are collected in Table IV. The value $\rho = 0$ for all the complexes $Cu(C_6O_4X_2)L_2$ deserves discussion; all the magnetic studies were carried out in the 3.8–300 K temperature range, except for $Cu(C_6O_4Cl_2)(NH_3)_2$ for which the study was extended down to 1.2 K. The magnetic susceptibility exhibits a maximum around 3.3 K characteristic of a weak antiferromagnetic coupling. For this latest compound, the best fitting in the 1.2–4.2 K range as well as in the 1.2–300 K range is obtained for a negligible value of ρ. Most likely, this does not mean that $Cu(C_6O_4Cl_2)(NH_3)_2$ has an exceptional magnetic purity, without detectable amount of ends of chains or of noncoupled Cu(II). This surprising behavior could result from an effect that we have not considered such as an antiferromagnetic interchain interaction, which would compensate in some way the effect of ρ. Since all the $Cu(C_6O_4X_2)L_2$ compounds were prepared in the same way and have probably the same structure, we decided to fix $\rho = 0$ when interpreting their magnetic properties. As an example, the experimental magnetic data and the best fitting curves for $Cu(C_6O_4Br_2)$ are plotted in Figure 5 and for $Cu(C_6O_4Cl_2)(NH_3)_2$ and $Cu(C_6O_4Cl_2)(py)_2$ in Figure 6. The examination of Table IV leads to the following observations: (i) Although there is a large intrachain Cu–Cu distance between nearest neighbors, about 7.5 Å, in $Cu(C_6O_4X_2)$, the coupling is far from being negligible. J is equal to −24.5 and −22.3 cm^{-1} for X = Cl and Br, respectively. (ii) The fixation of two nitrogen-containing ligands per copper atom leads to a drastic decrease of the intrachain antiferromagnetic coupling: J is equal to −24.5 cm^{-1} for $Cu(C_6O_4Cl_2)$ and to only −3.8 cm^{-1} for $Cu(C_6O_4Cl_2)(NH_3)_2$. (iii) The nature of the halogen plays a minor role: the magnetic properties of $Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Br_2)$ are quite similar. In the same way, the magnetic properties of $Cu(C_6O_4Cl_2)(NH_3)_2$ are very close to those of $Cu(C_6O_4Br_2)(NH_3)_2$. (iv) As for the magnetic behaviors, two groups may be distinguished among the $Cu(C_6O_4X_2)L_2$ compounds: those for which $|J|$ is the range 3.6–3.8 cm^{-1} and those for which the coupling is still weaker with $|J|$ in the range 1.5–2.1 cm^{-1}. To the former group belong the compounds $Cu(C_6O_4Cl_2)L_2$ with L = NH_3, im, and $Cu(C_6O_4Br_2)(NH_3)_2$; to the latter, the compounds $Cu(C_6O_4Cl_2)L_2$ with L = py, anil, bzim, and 2-Meim.

Table IV. Best Fitting Magnetic Parameters for the $Cu(C_6O_4X_2)$ and $Cu(C_6O_4X_2)L_2$ Compounds Studied in This Work

compd	J/cm^{-1}	g	ρ	R/Å
$Cu(C_6O_4Cl_2)$	−24.5	2.16	0.079	2.4×10^{-4}
$Cu(C_6O_4Br_2)$	−22.3	2.13	0.078	2.4×10^{-4}
$Cu(C_6O_4Cl_2)(NH_3)_2$	−3.8	2.06	0	2.7×10^{-3}
$Cu(C_6O_4Br_2)(NH_3)_2$	−3.8	2.12	0	1.2×10^{-3}
$Cu(C_6O_4Cl_2)(im)_2$	−3.7	2.12	0	1.4×10^{-3}
$Cu(C_6O_4Cl_2)(py)_2$	−1.8	2.21	0	9.2×10^{-4}
$Cu(C_6O_4Cl_2)(anil)_2$	−1.8	2.26	0	4.4×10^{-4}
$Cu(C_6O_4Cl_2)(bzim)_2$	−2.0	2.24	0	1.1×10^{-3}
$Cu(C_6O_4Cl_2)(2\text{-}Meim)_2$	−1.5	2.20	0	5.4×10^{-4}

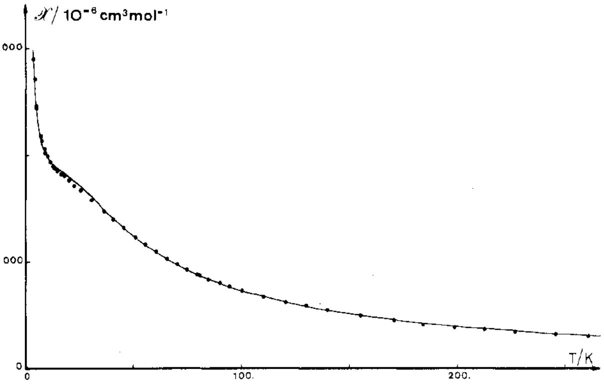

Figure 5. Experimental (points) and fitted (curve) temperature dependences of the magnetic susceptibility for $Cu(C_6O_4Br_2)$.

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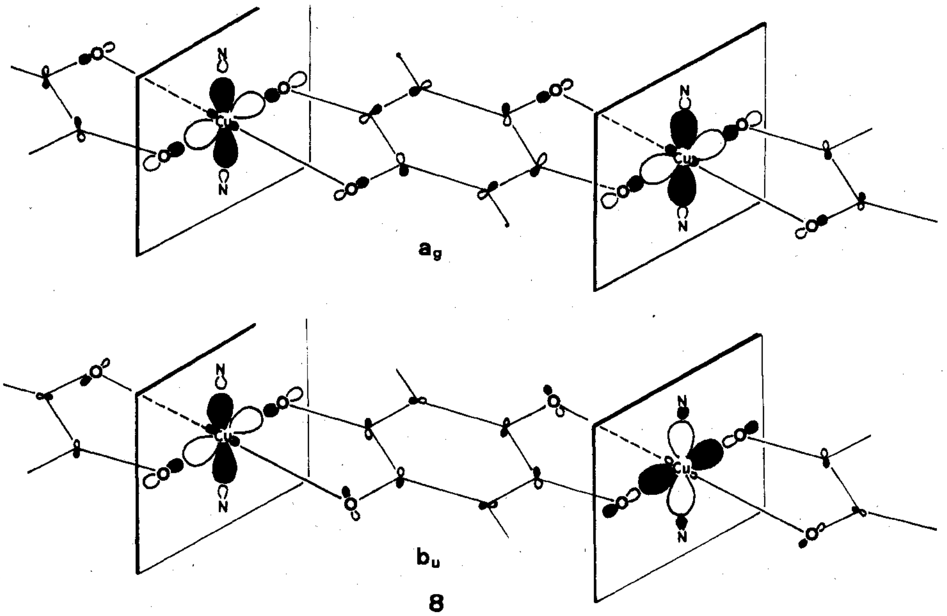
(24) J. Garaj, M. Langfelderova, G. Lundgren, and J. Gazo, *Collect. Czech. Chem. Commun.*, **37**, 3181 (1972).

(25) W. E. Estes, D. P. Gavel, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **17**, 1415 (1978).



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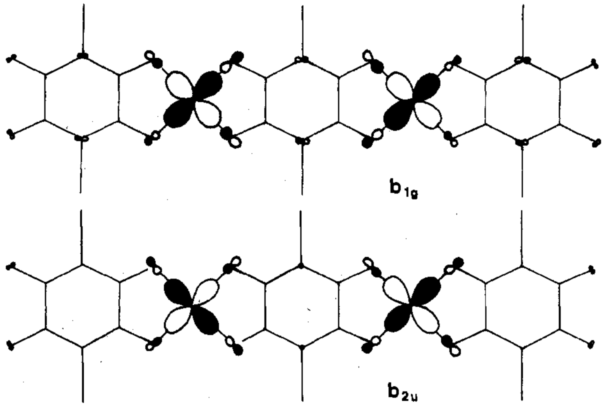
We now propose an orbital interpretation for each of the observations above: (i) It has been established[26] that the J exchange parameter in magnetic linear chains may be expressed as the sum of an antiferromagnetic contribution J_{AF} and of a ferromagnetic contribution J_F. J_{AF} and J_F are given respectively by

$$J_{AF} = -\frac{1}{n^2}\sum_{\mu=1}^{n}\Delta_\mu S_{\mu\mu} \qquad J_F = \frac{1}{n^2}\sum_{\mu,\nu=1}^{n} J_{\mu\nu}$$

in which n is the number of paramagnetic electrons per center, $S_{\mu\mu}$ is the overlap integral between two magnetic orbitals of the same symmetry μ centered on nearest-neighbor transition ions, Δ_μ is the width of the molecular orbital band built from the magnetic orbitals of symmetry μ for the spectroscopic term of highest spin multiplicity, $J_{\mu\nu}$ is the two-electron-exchange integral between magnetic orbitals of symmetry μ and ν, respectively, centered on nearest-neighbor ions. Moreover, it has been shown that Δ_μ in a $(M-X)_n$ chain may be evaluated from the δ_μ gap between the molecular orbitals of highest and lowest energies, respectively, built from the same magnetic orbitals in the hypothetical binuclear complex X–M–X–M–X.[26] The relation is then $\Delta_\mu = 2\delta_\mu$. Finally $S_{\mu\mu}$, in first-order approximation, is proportional to Δ_μ so that J_{AF} varies as $-\Delta_\mu^2$ or $-\delta_\mu^2$. In the discussion which follows, we shall focus on J_{AF}. Two reasons of different nature explain this limitation: on the one hand, the influence of the structural factors on the magnitude of J_F is not yet well known; on the other hand, in polymeric systems with extended polyatomic bridging ligands such as $(C_6O_4X_2)^{2-}$, each magnetic orbital $\phi_{\mu i}$ is delocalized on a large number of bridging atoms so that the spin density on each atom is weak. The overlap density $\rho_\mu = \phi_{\mu i}\phi_{\mu i+1}$ between magnetic orbitals centered on nearest-neighbor metallic ions is spread out and weak among all the bridging atoms. It turns out that the overlap integral $\int_{\text{space}}\rho_\mu(1)\,d\tau_1$ which governs the magnitude of the antiferromagnetic contribution may be important whereas the two-electron-exchange integral $\int_{\text{space}}[[\rho_\mu(1)][\rho_\mu(2)]\,d\tau_1\,d\tau_2/r_{12}]$ governing the magnitude of the ferromagnetic contribution will remain very weak. This difficult and important problem will be studied in a future paper.[27] In $Cu(C_6O_4X_2)$, each magnetic orbital is built from the $d_{x^2-y^2}$ metallic orbital pointing toward the oxygen atoms bound to copper. The magnitude of J_{AF} is related to the energy gap between the b_{1g} and b_{2u} molecular obitals in the hypothetical binuclear entity $[Cu_2(C_6O_4X_2)_3]^{2-}$. These MO's obtained by extended Hückel calculation are shown in **5**. The oxygen–carbon overlaps of the type O1–C2 (see **3**) are negative in b_{1g} and positive in b_{2u}, so that b_{1g} is destabilized with regard to b_{2u}. The energy difference δ between both MO's is responsible for the observed antiferromagnetic coupling. The EH calculation of δ, carried out with the parametrization already used in ref 3 and by replacing the halogen X by a pseudohydrogen with a 1s orbital energy equal to −18.1 eV led to δ = 0.0666 eV. Perhaps it is not unuseful to point out that the π system of the $(C_6O_4X_2)^{2-}$ ion does not



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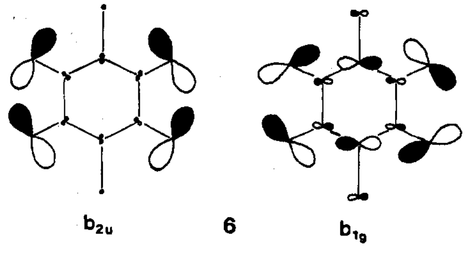

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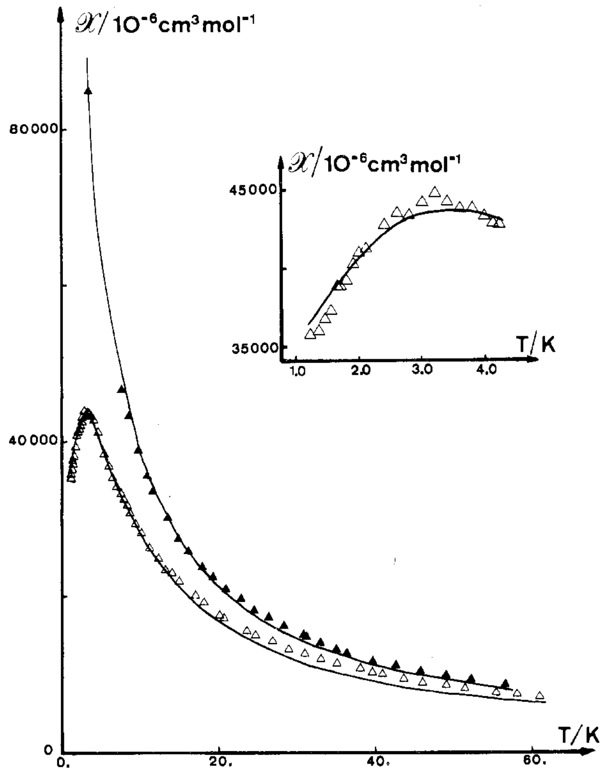
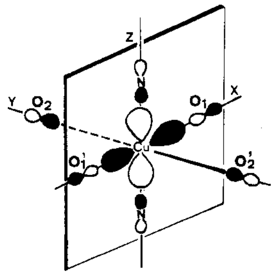


Figure 6. Experimental (points) and fitted (curves) temperature dependences of the magnetic susceptibility for $Cu(C_6O_4Cl_2)(NH_3)_2$ (△) and $Cu(C_6O_4Cl_2)(py)_2$ (▲).

occur in the exchange interaction. The phenomenon is purely σ in nature. This interpretation of the exchange interaction in $Cu(C_6O_4X_2)$ very deeply differs from that proposed by Sartene et al. some years ago.[28] (ii) the negligible influence of the nature of X on the magnetic properties may be easily interpreted. In the last occupied σ MO's of the chloranilato ion which interact with the $d_{x^2-y^2}$ metallic orbitals (see **6**), the contributions of the chlorine orbitals are very weak. If in the calculation concerning $[Cu_2(C_6O_4X_2)_3]^{2-}$ we vary the orbital energy of the pseudohydrogen to simulate an electronegativity variation of X, we find that δ remains essentially constant. (iii) The most interesting feature of this magnetic study is the drastic decrease of the interaction when nitrogen-containing ligands are fixed on the copper. This variation of J is related to the modification of the copper surrounding. The four nearest neighbors of each copper are no longer oxygen atoms, but two oxygen atoms (O1 and O1′) and two nitrogen atoms (see **7**). It turns out that each magnetic orbital undergoes



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a reversal of 90° around the O1–Cu–O1′ axis in order to point again toward the nearest neighbors. This orientation of the magnetic orbitals is particularly unfavorable to propagate the interaction along the chain. In fact, the situation is somewhat less dramatic. Owing to the actual site symmetry for copper, D_{2h} or below, the metallic contribution to the magnetic orbital is most purely $d_{x^2-y^2}$ but involves a small admixture of d_{z^2} pointing along the O2–Cu–O2′ axis (see **7**). Therefore, the spin density on the O2 and O2′ oxygen atoms is not exactly zero; this accounts for the very small residual coupling. To visualize this phenomenon of orbital reversal, we draw in **8** the two molecular orbitals built from the magnetic orbitals in the hypothetical binuclear complex $[Cu_2(C_6O_4X_2)_3(NH_3)_4]^{2-}$ as obtained by the EH calculation. The δ energy gap between these two MO's was found equal to 0.0411 eV, i.e., as expected, weaker than in $[Cu_2(C_6O_4Cl_2)_3]^{2-}$. However, the ratio $J[Cu(C_6O_4Cl_2)]/J[Cu(C_6O_4Cl_2)(NH_3)_2]$ is larger, in absolute value, than the ratio $\delta[Cu_2(C_6O_4Cl_2)_3{}^{2-}]^2/\delta[Cu_2(C_6O_4Cl_2)_3(NH_3)_4{}^{2-}]^2$. Owing to the poor knowledge of the actual bond lengths and angles in the diammino compound and to the roughness of the EH method, this discrepancy is far from being surprising. (iv) The reasons for which the values of J in $Cu(C_6O_4X_2)L_2$ compounds apparently lie in two ranges, either $J \approx -3.8$ cm⁻¹ or $J \approx -1.8$ cm⁻¹, are not clear for us. The EXAFS sectra of $Cu(C_6O_4Cl_2)(NH_3)_2$ ($J = -3.8$ cm⁻¹) and $Cu(C_6O_4Cl_2)(py)_2$ ($J = -1.8$ cm⁻¹) are quite similar. This result could arise from small differences in the strength of the bases L which would modify the residual spin densities on the O2 and O2′ atoms and hence the magnitude of the intrachain coupling. The observed magnetic behavior could also come from interchain interactions which would vary according to the nature of the base.

Conclusion

In this last part, we will discuss briefly the whole of the available results concerning the magnetic properties of the complexes with the bridging ligands $(C_6O_4X_2)^{2-}$, X being H or Cl. These results are collected in Table V. From this table, the following observations may be made: (i) The antiferromagnetic coupling is far weaker in the copper(II) binuclear complexes than in the chains $Cu(C_6O_4X_2)$. In $[Cu_2(C_6O_4Cl_2)(Me_5dien)_2](BPh_4)_2$, the surrounding of the copper is approximately square pyramidal with N_3O in the basal plane and an oxygen atom of the chloranilato ion at the apex. Thus, the basal plane of the pyramid is perpendicular to the chloranilato plane. It turns out that the orientation of the magnetic orbitals pointing toward the four atoms of the N_3O basal plane is unfavorable for transmitting the interaction between the metallic centers. As for the complexes with dpt as terminal ligands, their structures are unknown. However, it is probable that the square-pyramidal surrounding of each copper is distorted in such a manner that the spin density on the apex is increased with regard to the situation in $[Cu_2(C_6O_4Cl_2)(Me_5dien)_2](BPh_4)_2$. We may conclude that the σ-exchange pathway realized in the $Cu(C_6O_4X_2)$ compounds has a quite specific efficiency. (ii) To compare the magnitude of the exchange interaction in compounds with different metallic ions, we may calculate Jn^2 which, neglecting the ferromagnetic contribution, is equal to $-2\sum_{\mu=1}^{n}\delta_\mu S_{\mu\mu}$. Restricting ourselves to compounds in which the σ-exchange pathway is operative, we obtain −19.5 cm⁻¹ for $Cu(C_6O_4H_2)$, −8.8 cm⁻¹ for $[Ni_2(C_6O_4H_2)(tren)_2](BPh_4)_2$, −100 cm⁻¹ for $Fe_2(C_6O_4H_2)_3(H_2O)_4$, −24.5 cm⁻¹ for $Cu(C_6O_4Cl_2)$, −14.4 cm⁻¹ for $[Ni_2(C_6O_4Cl_2)(tren)_2](BPh_4)_2$, and −50 cm⁻¹ for $Fe_2(C_6O_4Cl_2)_3(H_2O)_4 \cdot 4H_2O$. The antiferromagnetic coupling appears to follow the sequence Fe(III) compounds > Cu(II) compounds > Ni(II) compounds. For the Ni(II) compounds, Jn^2 is given by $-2[\delta_{x^2-y^2}S_{x^2-y^2x^2-y^2} + \delta_{z^2}S_{z^2z^2}]$. Owing to the orientation of the d_{z^2} type magnetic orbitals, the term $\delta_{z^2}S_{z^2z^2}$ is expected to be very weak, so that the $d_{x^2-y^2}$ σ-exchange pathway appears to be more efficient in Cu(II) compounds than in Ni(II) compounds. As far as the Fe(III) compounds are concerned,

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Table V. Exchange Interaction Parameters ($\mathcal{H} = -J\hat{S}_i \cdot \hat{S}_j$) for the Compounds with the Bridging Ligands $(C_6O_4X_2)^{2-}$, with X = H, Cl[a]

ion	compd	*S*	*J*/cm⁻¹	ref
	Binuclear Complexes			
Cu(II)	$Cu_2(C_6O_4H_2)(Me_5dien)_2(BPh_4)_2$	$^1/_2$	±0.2	18
	$Cu_2(C_6O_4H_2)(dpt)_2(BPh_4)_2$	$^1/_2$	−9.2	18
	$Cu_2(C_6O_4Cl_2)(Me_5dien)_2(BPh_4)_2$	$^1/_2$	±0.2	18
	$Cu_2(C_6O_4Cl_2)(dpt)_2(BPh_4)_2$	$^1/_2$	−4.0	18
Ni(II)	$Ni_2(C_6O_4H_2)(tren)_2(BPh_4)_2$	1	−2.2	18
	$Ni_2(C_6O_4Cl_2)(tren)_2(BPh_4)_2$	1	−3.6	18
Fe(II)	$Fe_2(C_6O_4H_2)_3(H_2O)_4$	$^5/_2$	−4.0	29
	$Fe_2(C_6O_4Cl_2)_3(H_2O)_4 \cdot 4H_2O$	$^5/_2$	−2.0	29
	Chains			
Cu(II)	$Cu(C_6O_4H_2)$	$^1/_2$	−19.5	9
	$Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Cl_2)L_2$	*b*	*b*	this work
Fe(II)	$Fe(C_6O_4H_2)(H_2O)_2$	2	−2.8	29
	$Fe(C_6O_4Cl_2)(H_2O)_2$	2	−0.2	29

[a] Abbreviations: Me_5dien = 1,1,4,7,7-pentamethyldiethylenetriamine; dpt = dipropylenetriamine; tren = 2,2′,2″-triaminotriethylamine; BPh_4 = tetraphenylborate. [b] See Table IV.

the apparently weak accuracy on the exchange parameter determination should lead to some prudence in the interpretation of the magnetic properties. Nevertheless the magnitude of the antiferromagnetic coupling could be related to the efficiency of the d_{yz} and d_{zx} π-exchange pathways in addition to the $d_{x^2-y^2}$ σ-exchange pathway. (iii) Finally the inadequacy of the Heisenberg Hamiltonian to describe the exchange interaction between orbitally degenerate ions prohibits any discussion on the results concerning the Fe(II) compounds.

Acknowledgment. We are grateful to Dr. R. Fourme for helpful discussions. We thank Dr. J. P. Renard for his aid in the magnetic measurements in the range 1.2–4.2 K and Dr. P. C. Marin and his collaborators from the LAL (Laboratoire de l'Accélérateur Linéaire at Orsay), who operated the storage ring D.C.I.

Registry No. $Cu(C_6O_4Cl_2)$, 29504-40-3; $Cu(C_6O_4Br_2)$, 27882-04-8; $Cu(C_6O_4Cl_2)(NH_3)_2$, 74482-51-2; $Cu(C_6O_4Cl_2)(py)_2$, 74482-53-4; $Cu(C_6O_4Cl_2)(anil)_2$, 74482-55-6; $Cu(C_6O_4Cl_2)(2\text{-}Meim)_2$, 74482-57-8; $Cu(C_6O_4Cl_2)(bzim)_2$, 74482-59-0; $Cu(C_6O_4Cl_2)(im)_2$, 74482-61-4; $Cu(C_6O_4Br_2)(NH_3)_2$, 74482-63-6.

Supplementary Material Available: Some experimental EXAFS spectra in *k* and *R* space, *k* and *R* filtered spectra and fittings, and *R*-space simulated spectra (15 pages).[30] Ordering information is given on any current masthead page.

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(30) *k*- and *R*-space spectra of $Cu(C_6O_4Cl_2)(NH_3)_2$, $CuC_2O_4 \cdot {}^1/_3H_2O$, and $CuC_2O_4(NH_3)_2 \cdot 2H_2O$, *R*-space filtered spectra for the bromine shells in $Cu(C_6O_4Br_2)$, and *R*-space simulated spectra of $Cu(C_6O_4Br_2)$ are given as supplementary material.

(31) A tetrahedral environment of copper in CuX_4 is known when X is a halogen. This is very rare in CuO_4. We found only one well-documented case: $CuCr_2O_4$, a spinel structure where copper(II) lies in a distorted tetrahedral environment (see ref 19, p 493). Moreover, a copper(II) chain with a 90° twisted bromanilato bridging ligand would lead to orthogonal magnetic orbitals and consequently to an intrachain ferromagnetic coupling. See, for instance, O. Kahn, J. Galy, P. Tola, and H. Coudanne, *J. Am. Chem. Soc.*, **100**, 3931 (1978).

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Photochemistry of the Cyanopentaamminechromium(III) Ion

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Ligand field (LF) irradiation of the $Cr(NH_3)_5(CN)^{2+}$ ion in acidic aqueous solution leads to exclusive aquation of NH_3, while only CN^- is released thermally. The quantum yields (Φ = 0.33 mol einstein^{-1}) are wavelength independent throughout the LF region. Unlike the other acidopentaammines of chromium(III), the lowest quartet excited state of this complex is $^4B_2$, with equatorial antibonding character. Photolabilization of NH_3 can be accounted for by Adamson's rules and by various theoretical models. The possible involvement of the upper ^4E state is discussed. The photoproduct $Cr(NH_3)_4(H_2O)(CN)^{2+}$ consists of a mixture of cis and trans isomers in a ca. 2:1 ratio. Equatorial photoaquation is suggested to occur with partial stereochemical change. NH_3 loss is the only photoreaction also upon charge-transfer (CT) excitation. The quantum yields and the product distribution are virtually the same as in the LF photolysis, indicating efficient conversion of CT (metal-to-ligand) states to LF ones.

Introduction

The photolytic behavior of $Cr(NH_3)_5X^{2+}$-type ions upon ligand field (LF) excitation continues to be the subject of thorough investigation.[1] Thus far, relevant results have been gathered for X = Cl,[2-4] NCS,[5,6] Br,[7] N_3,[8] OCOR,[9] and F.[10,11] These have significantly contributed to the development of semiempirical[12] and theoretical[13-18] models that account for ligand labilization in terms of the antibonding properties of the lowest quartet excited state. In all the above systems (including the controversial case of X = F)[19,20] such a state is ^4E and is associated with a predominant d_{z^2} antibonding character, i.e., with preferential bond weakening along the NH_3–X direction.

In order to explore the photochemistry of an uncommon member of this family, we have recently synthesized and

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