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Magnetic and Spectroscopic Properties of Transition Metal Coordination Polymers with Aminophosphonic Acids. I. Magnetic Properties of some Copper(II) Complexes of Aminomethylphosphonic and Aminoethylphosphonic Acids

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The solid compounds formed between the aminomethylphosphonic or aminoethylphosphonic acids and the copper(II) ion in monocrystalline and polycrystalline form were synthesized and characterized by magnetic susceptibilities value data obtained by the Faraday method over the temperature range from 4.2 K to 300 K and by providing a model of magnetic interactions. Structures which are compatible with the magnetic data are suggested for the complexes.

Introduction

Exchange interactions responsible for ferro- and antiferromagnetism occur quite frequently in the complexes of aminocarboxylic acids with the transition metal ions [1–6]. A similar effect may occur in the transition metal compounds with the aminomethylphosphonic acid AMPh [$H_2NCH_2PO_3H_2$] and aminoethylphosphonic acid AEPh [$H_2NCH(CH_3)PO_3H_2$], the structural analogues of glycine (Gly) [$H_2NCH_2CO_2H$] and α-alanine (α-Ala) [$H_2NCH(CH_3)CO_2H$] respectively. In the present paper we are dealing with magnetic properties of the copper(II) complex compounds with aminomethylphosphonic or aminoethylphosphonic acids.

Experimental

$Cu(AMPh)2H_2O$ was prepared in the polycrystalline form by mixing 5 millimol of aminomethylphosphonic acid, brought previously to pH 11.5 by means of 1 *M* sodium hydroxide solution, with 2.5 millimol of cupric chloride. The final pH value of such a mixture is 10.5. Under such conditions the coordination polymer of Cu(II) does not form. Afterwards the pH value was brought to 4 by means of 1 *M* hydrochloric acid solution and the mixture was heated to 323–333 K, to yield the yellow-green compound.

$Cu(AMPh)_2$ was synthesized in the monocrystalline form by very slow evaporation of water from the aqueous solution of 5 millimol of aminomethylphosphonic acid and 2.5 millimol of cupric chloride, which had been prepared as above at room temperature, the final pH value being 4.

$Cu(AMPh)ClH_2O$ was also synthesized in the polycrystalline form by mixing 5 millimol of aminomethylphosphonic acid, brought previously to pH 9.4 by means of 0.5 *M* sodium hydroxide solution, with 5 millimol of cupric chloride (final pH is 8.3). The mixture was heated for 1.5 hours in water bath at 323–333 K to yield a green-blue product.

$Cu(AEPh)2H_2O$ was prepared in the polycrystalline form by mixing 10 millimol of aminoethylphosphonic acid, brought previously to pH 10 by means of 1 *M* sodium hydroxide solution, with 10 millimol of cupric chloride. The blue compound was synthesized.

The percentage contents of phosphorus, nitrogen and chlorine in the prepared compounds were determined by normal elemental analysis, whereas the copper content was determined by titration with standard 0.001 *M* EDTA solution. The results of analysis are summarized in Table I. Electronic and molecular structures were investigated by electronic absorption and vibrational spectroscopy methods [17].

Results and Discussion

The magnetic properties were investigated by magnetic susceptibility measurements by the Faraday method over the temperature range from 4.2 to 300 K in the 6 kOe magnetic field and by providing the model of magnetic interactions. Magnetic susceptibilities were measured for several compounds of the same molecular formula, synthesized independently under the same conditions. The molar susceptibilities

TABLE I. Analysis of Cu(AMPh)2H_2O, Cu(AMPh)ClH_2O, Cu$(AMPh)_2$ and Cu(AEPh)2H_2O.

Compound	P, %		N, %		Cl, %		Cu, %	
	Found	Calc	Found	Calc	Found	Calc	Found	Calc
Cu(AMPh)2H_2O	15.15	14.85	6.9	6.7	–	–	30.2	30.46
Cu(AMPh)ClH_2O	13.44	13.64	5.59	6.17	15.3	15.62	28.3	27.99
Cu$(AMPh)_2$	22.0	21.84	9.9	9.88	–	–	22.4	22.405
Cu(AEPh)2H_2O	13.7	13.913	6.4	6.29	–	–	28.19	28.54

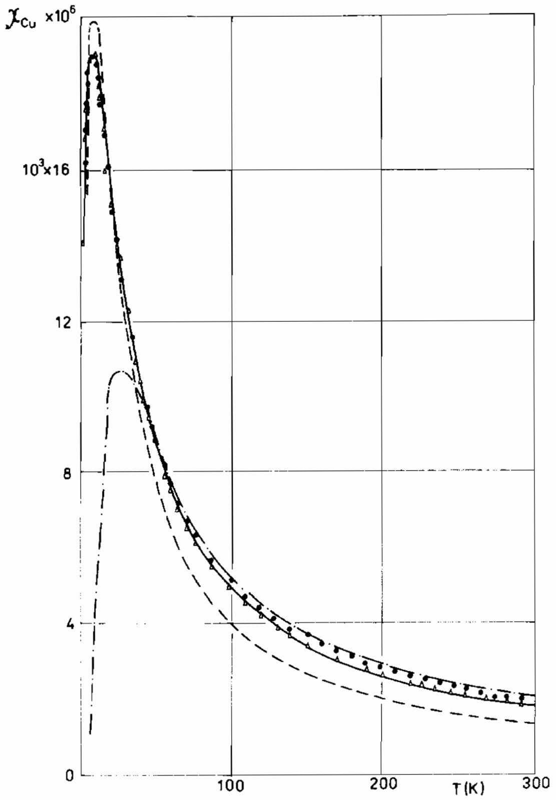

Fig. 1. Plot of magnetic susceptibility *versus* temperature for Cu(AMPh)2H_2O; Δ, ● experimental values; –.–.– values determined from formula (3) for g = 2.367, 2J = –19.85 cm^{-1}; ——— values determined from formula (5) for g = 2.35, J = –4.257 cm^{-1}; – – – values determined from formula (3) for g = 2.13, 2J = –11.9 cm^{-1}.

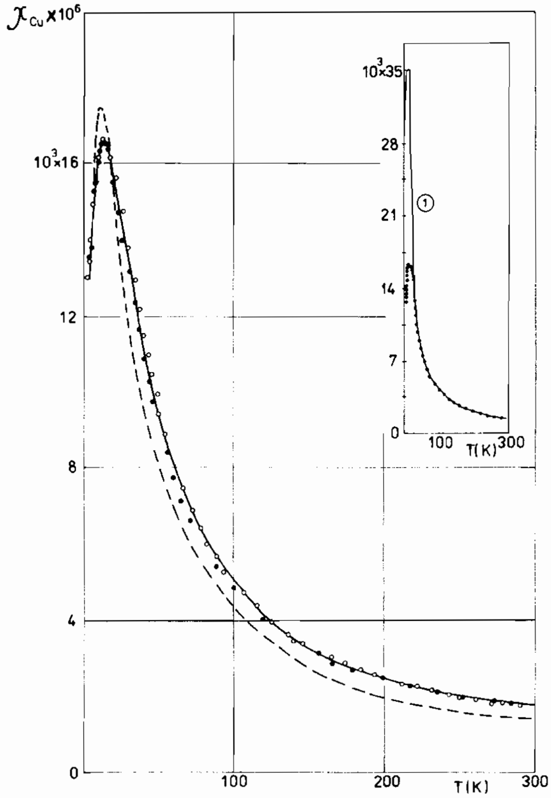

Fig. 2. Plot of magnetic susceptibility *versus* temperature for Cu(AMPh)ClH_2O; ○, ● experimental values; ——— values determined from formula (5) for g = 2.48, J = –5.249 cm^{-1}; – – – – values determined from formula (3) for g = 2.2, 2J = –14.5 cm^{-1}; —①— values determined from formula (3) for g = 2.273, 2J = –7.42 cm^{-1}.

were corrected for diamagnetic effects. The magnetic data of Cu(AMPh)2H_2O, Cu(AMPh)ClH_2O and Cu(AEPh)2H_2O are presented in diagrams of magnetic susceptibilities against temperature as shown in Figures 1, 2 and 6. The plots of reciprocal magnetic susceptibility against temperature for Cu(AMPh)2H_2O, Cu$(AMPh)_2$, Cu(AMPh)ClH_2O and Cu(AEPh)2H_2O are provided in Figures 3, 4 and 7. For the compounds Cu(AMPh)2H_2O, Cu(AMPh)ClH_2O and Cu(AEPh)2H_2O which satisfy the Curie–Weiss law, the plots of effective magnetic moments *versus* temperature are also provided in Figures 3, 4 and 7. The effective magnetic moments were calculated from the formula

$$\mu_{eff} = 2.83\,[\chi_{Cu}^{Corr}(T - \theta)]^{1/2}$$

From the values of magnetic susceptibilities, the following characteristic magnetic parameters were determined: θ, T_N, $\chi_{max}(T_N)$, $\chi(T)$, C (Table II). The values of the Weiss constant θ indicate exchange interactions which are responsible for antiferromagnetism of Cu(AMP)2H_2O (θ = –13 K) and of

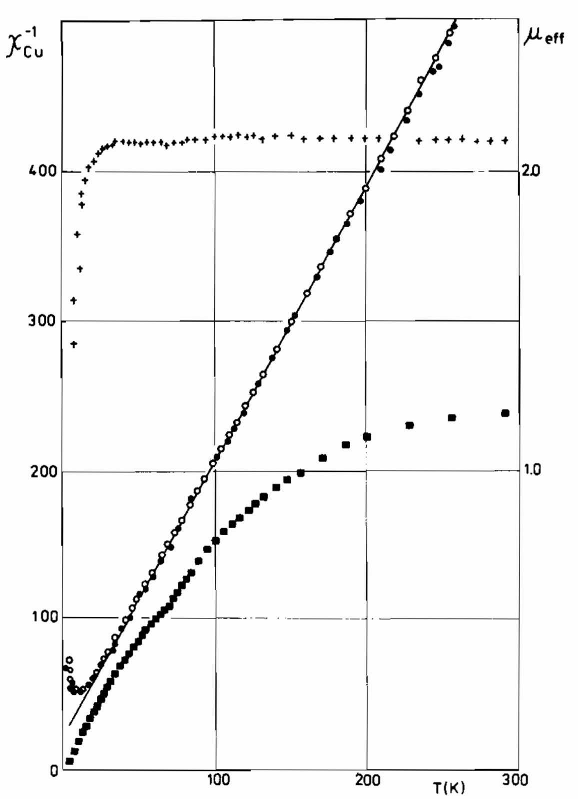

Fig. 3. Plot of reciprocal magnetic susceptibility *versus* temperature for Cu(AMPh)2H_2O and $Cu(AMPh)_2$; ○, ● experimental values for Cu(AMPh)2H_2O; ■ experimental values for $Cu(AMPh)_2$; ——— values determined from formula (2) for Cu(AMPh)2H_2O; + plot of effective magnetic moments *versus* temperature for Cu(AMPh)2H_2O.

Cu(AMPh)ClH_2O (θ = −4 K) as well as Cu(AEPh)-2H_2O (θ = −15 K) at low temperatures. Magnetic susceptibilities of Cu(AMPh)2H_2O and Cu(AMPh)-ClH_2O is of the paramagnetic order and varies specifically with temperature, exhibiting a sharp maximum at the so-called Néel point, T_N (Figures 1, 2; Table II). The compounds under investigation have the following Néel points: 10.8 K for Cu(AMPh)2H_2O and 15.3 K for Cu(AMPh)ClH_2O. Above T_N the magnetic susceptibilities of these compounds satisfy the Curie–Weiss law.

$$\chi = \frac{C}{T - \theta} \tag{1}$$

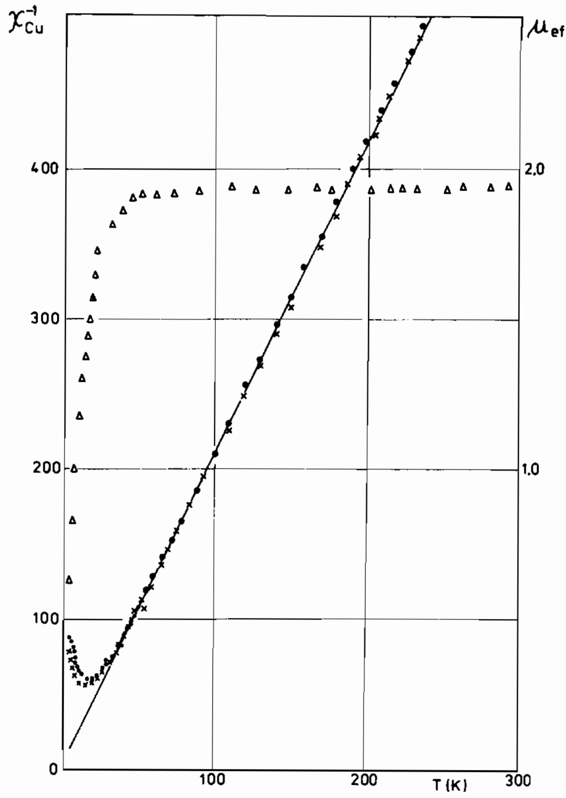

Fig. 4. Plot of reciprocal magnetic susceptibility *versus* temperature for Cu(AMPh)ClH_2O; ●, X experimental values; ——— values determined from formula (2); Δ plot of effective magnetic moments *versus* temperature.

Below T_N the magnetic susceptibilities decrease with the decrease in temperature. Magnetic susceptibilities determined for the temperatures $T > T_N$ according to the formula

$$\chi = \frac{0.550}{T + 13} \tag{2A}$$

for Cu(AMPh)2H_2O over the temperature range from 35 K to 290.5 K and according to the equation

$$\chi = \frac{0.487}{T + 4} \tag{2B}$$

for Cu(AMPh)ClH_2 over the temperature range from 32 K to 292 K and according to:

TABLE II. Values of Magnetic Parameters θ, T_N, $\chi_{max}(T_N)$, $\chi(T)$, C.

Compound	θ (K)	T_N (K)	$\chi_{max}(T_N)$	χ(9 K)	χ(292 K)	C
Cu(AMPh)2H_2O	−13	10.8	0.019379	0.018868	0.001780	0.55
Cu(AMPh)ClH_2O	−4	15.3	0.016684	0.015105	0.001627	0.487
$Cu(AMPh)_2$	+0.2	–	–	0.058709	0.004182	–
Cu(AEPh)2H_2O	−15	–	–	0.026314	0.001736	0.533

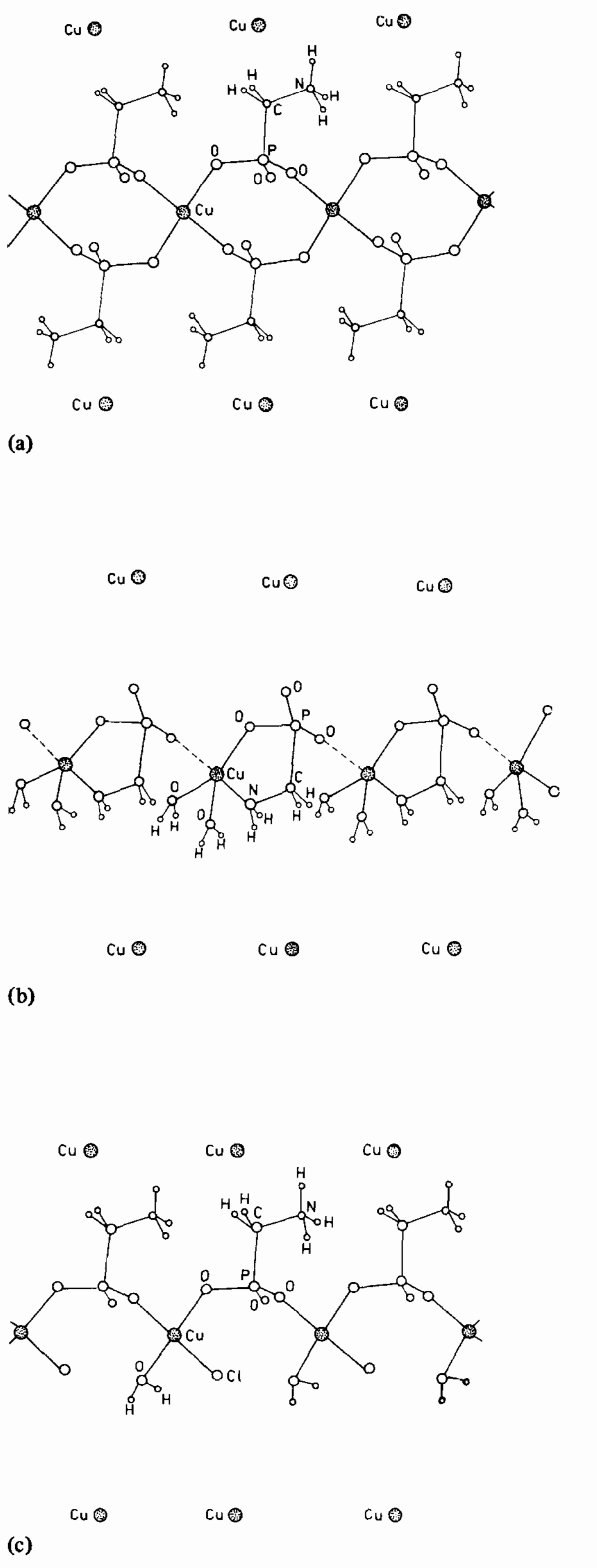

Fig. 5. Structures of compounds; (a) $Cu(AMPh)_2$ determined by X-ray [11]; (b) $Cu(AMPh)2H_2O$, suggested; (c) $Cu(AMPh)ClH_2O$, suggested.

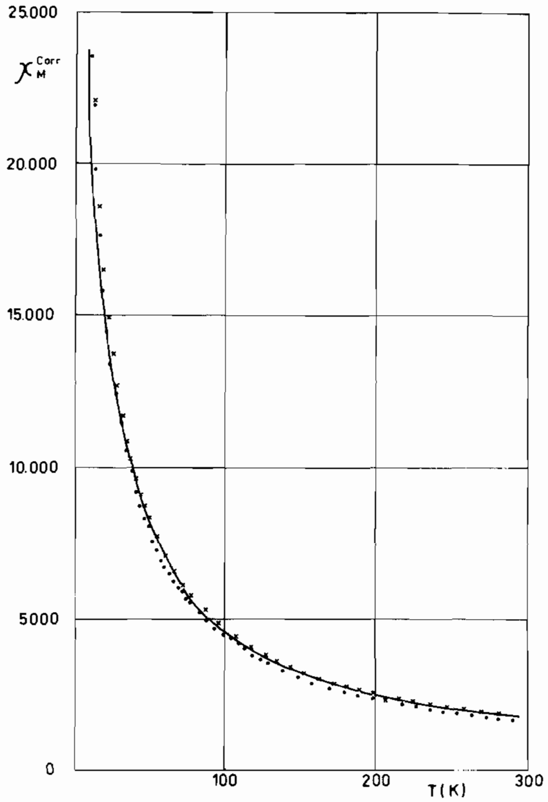

Fig. 6. Plot of magnetic susceptibility *versus* temperature for $Cu(AEPh)2H_2O$; ●, X experimental values; ——— values determined from formula (2).

$$\chi = \frac{0.533}{T + 15} \tag{2C}$$

for $Cu(AEPh)2H_2O$ over the temperature range from 22 K to 297 K are consistent with the experimental values (Figures 3, 4, 6, 7). The experimental values of the following specific magnetic parameters: θ, T_N, $\chi_{max}(T_N)$, $\chi(T)$, C (Table II) suggest the necessity of the calculations of the theoretical magnetic susceptibilities. The compounds under investigation were assumed to contain the intramolecular magnetic interactions, the same as in copper tirosinate isolated magnetic dimeric systems, in which magnetic interactions between the two adjacent paramagnetic ions are considered, without more remote neigbours taken into account [1]. In such a system the magnetic susceptibilities may be described by the following formula:

$$\chi_{Cu} = \frac{3K}{T}\left[\frac{1}{3 + x^2}\right] + N\alpha$$

where (3)

$$x = \exp(-J/kT)$$

$$K = \frac{Ng^2\beta^2}{3k}$$

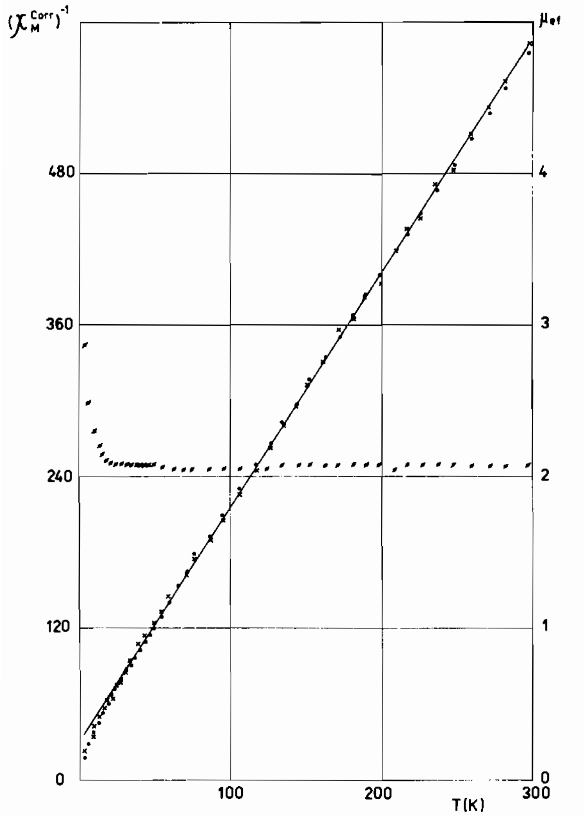

Fig. 7. Plot of reciprocal magnetic susceptibility *versus* temperature for Cu(AEPh)2H$_2$O; ●, X experimental values; ——— values determined from formula (2); ●● plot of effective magnetic moments *versus* temperature.

The values used for the magnetic parameters were obtained using the best fitting procedure in which the values of 2J and g were changed for the equal value of the best fitted parameter A_{BF}, as defined in the equation (4). Calculations were performed on a RIAD computer by the gradient method

$$A_{BF} = \sum_{i=1}^{n} [(\chi_i)_{exp} - \chi(T_i)_{calc}]^2 \tag{4}$$

The calculated values of magnetic susceptibilities consistent with the experimental values were obtained over the temperature range from 40 K to 300 K by fitting parameters: g = 2.367 and 2J = –19.85 cm^{-1} with A_{BF} = 0.62 X 10^{-5} for Cu(AMPh)2H$_2$O; g = 2.273 and 2J = –7.42 cm^{-1} with A_{BF} = 0.2 X 10^{-4} for Cu(AMPh)ClH$_2$O (Figures 1 and 2). However between 4.2 K and 40 K large deviations are observed for experimental and theoretical data. By further fitting the g and 2J parameters it was possible to reach a better approximation of the calculated magnetic susceptibilities for the temperature range from 4.2 K to 40 K assuming g = 2.13, 2J = –11.9 cm^{-1} and A_{BF} = 0.73 X 10^{-5} for Cu(AMPh)2H$_2$O, and g = 2.20, 2J = –14.5 cm^{-1} with A_{BF} = 0.83 X 10^{-5} for Cu(AMPh)ClH$_2$O but it was much worse for the paramagnetic range (Figures 1 and 2). These results indicate that isolated dimeric magnetic systems, such as those observed in the complexes of aminocarboxylic acids with the copper(II) ion, are not created in the Cu(AMPh)2H$_2$O and Cu(AMPh)-ClH$_2$O compounds under investigation. The formula (3) has been successfully used for description of magnetic interactions in the copper(II) compounds with aminocarboxylic acids [1–6]. The tendency of the phosphonic group PO_3^{-2} to form polymeric systems is well known. The coordination polymers of the phosphonic acids [7, 8], alkylphosphinato [18, 19], phosphonate esters [9] and phenylphosphonic acids [10] have been already described. It was also demonstrated by X-ray analysis performed in our laboratory [11] that Cu(AMPh)$_2$ is a linear coordination polymer in which the adjacent copper ions are linked by two bridges –O–P–O– (Figure 5.1). We suppose that on this basis the magnetic properties of Cu(AMPh)2H$_2$O and Cu(AMPh)ClH$_2$O may be described by the following formula as depicting the magnetic properties of linear coordination polymers [12–16]:

$$\chi = 1/3\chi_{\parallel} + 2/3\chi_{\perp}$$

where:

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4J} X \exp(2X)$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8J} [\tanh X + X \operatorname{sech}^2 X] \tag{5}$$

$$X = \frac{2J}{kT}$$

Magnetic susceptibilities determined by this formula over the temperature range from 4.2 K to 300 K with g = 2.35 and 2J = –8.51 cm^{-1} with A_{BF} = 0.1 X 10^{-6} for Cu(AMPh)2H$_2$O and g = 2.48 and 2J = –10.50 cm^{-1} with ABF = 0.14 X 10^{-6} for Cu(AMPh)ClH$_2$O are in a good agreement with the experimental values (Figs. 1 and 2). This fact indicates that the spin interaction is within coordination polymers, but it is also not only the lattice ferro- or antiferromagnetic effect. The J values are negative and characterize these compounds as having a singlet ground state and the triplet state at 8.5 cm^{-1} above it for Cu(AMPh)2H$_2$O and at 10.5 cm^{-1} for Cu(AMPh)-ClH$_2$O. The distance between the two metal ions in these compounds equal to approximately 5 Å is too large for direct spin exchange or dipolar in contrast to the classical case of cupric acetate monohydrate, where the Cu–Cu distance is 2.64 Å, and there may be a direct metal–metal interaction (2J = –280

cm^{-1}). For Cu(AMPh)$2H_2O$ and Cu(AMPh)ClH_2O the superexchange mechanism via rather long and novel –O–P–O–bridge may apply to explain the data obtained. This is the first time that three (oxygen, phosphorus and oxygen) atoms act as the media for superexchange in the investigated Cu(AMPh)$2H_2O$ and Cu(AMPh)ClH_2O compounds. The exact pathway is probably via a *sigma* orbital mechanism with three intra-atomic direct exchange and interatomic electron transfer. In addition, θ is a constant that may contain any additional magnetic effects in the lattice. The small values of θ (–13 K, –4 K) indicate that there is a weak lattice antiferromagnetic effect which becomes prominent at low temperatures. The presence of these additional interactions can be noticed in the slight drop in the effective magnetic moments below 30 K, as shown in Figs. 3 and 4. Magnetic susceptibilities determined by formula (5) over the temperature range from 4.2 K to 300 K with $g = 2.70$ and $2J = -0.0148\ cm^{-1}$ with $A_{BF} = 0.7 \times 10^{-4}$ for Cu(AEPh)$2H_2O$ are not in a good agreement with the experimental values. This fact and the small value of J indicate that intramolecular exchange is weak. Besides there appears a weak lattice ferromagnetic effect which becomes appreciable at low temperatures. It can be noticed in the slight rise in the effective magnetic moments below 20 K, as shown in Fig. 7.

It is worth mentioning that for the compound $Cu(AMPh)_2$, the experimental magnetic susceptibility data are not fitted very well by the equation (5). The very high values of magnetic susceptibilities of $Cu(AMPh)_2$ suggest the different character of magnetic interactions, and this phenomenon is the object of our further study.

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