APPLICATION OF MAGNETIC METHODS TO THE STUDY
OF 3d TRANSITION METAL COMPLEXES

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ABSTRACT

On the basis of some theoretical considerations the dependence of the magnetic moment μ of complexes of 3d elements Ti, V, Cr, Mn, Fe, Co, Ni and Cu was studied as a function of the oxidation state of the elements, its coordination and crystal field strength. Examples of such relations are given to illustrate that valuable information can be obtained about the structure of the complexes of these elements with ligands used in pharmaceutical chemistry.
<u>Keywords:</u> magnetic methods, metal complexes.

INTRODUCTION

The magnetochemical methods are very important for the characterization of transition metal compounds. They permit determination of the transition element participating in the complex as well as its oxidation state, coordination and character of exchange interactions [1-5]. Magnetochemical methods are based on measurement of the temperature dependence of the magnetic susceptibility. That is why attention is paid to the possibility to characterize, using this dependence, complex compounds of 3d transition metals.

THEORETICAL

Paramagnetic susceptibility is present in substances where the elements participating in the compounds have a magnetic moment of their own. It is known that the presence of a magnetic moment depends on the electron structure of a given element or ion.

In the absence of interaction between the magnetic moments in a substance the following dependence is valid:

$$\chi_{mol} = N_a . \mu_{eff}^2 [3kT]^{-1} \tag{1}$$

Where μ_{eff} is the effective magnetic moment (the magnetic moment expressed in Bohr magnetons), N_a is the Avogadro number, k is the Boltzman constant and T is the temperature in K. This dependence is known as the Curie law and the quantity C is the Curie constant equal to

$$C = N_a \mu_B^2 [3k]^{-1} \mu_{eff}^2 \tag{2}$$

In the presence of interaction between the magnetic moments, the parameter θ is also included and the dependence can be written as

$$\chi_{mol} = C[T-\theta]^{-1} \tag{3}$$

This equation is known as the Curie -Weiss law, where θ is the so called Weiss constant which depends on the strength of interaction between the magnetic moments of the ions in the crystal and their coordination with respect to the surrounding neighbors.

When the crystal structure is formed, the magnetic moment of a given ion participating in this structure depends on the oxidation state, the symmetry and strength of the crystal field and the character of the chemical bond. This permits upon measuring the magnetic susceptibility and determining the magnetic moment, to analyze on these important parameters of a given transition metal complex.

On the basis of quantum mechanics, Van Fleck [6] calculated the theoretical dependence of the magnetic susceptibility and the magnetic moment on the oxidation state of the ion and the coordination and strength of the crystal field, in which this ion is located. These

theoretical relations show that, depending on the oxidation state and the coordination, two cases are possible.

In the first case the magnetic moment depends on temperature and, in general, this dependence may be described as follows:

$$\mu_{eff} = f(M^{n+}, CF, k, T, \lambda, \Delta) \qquad (4)$$

where M^{n+} is oxidation state of the 3d element, PF is the type of the crystal field , λ is a constant of spin orbital interaction and Δ takes into account the crystal field strength.

For octahedral coordination the crystal field could be strong or intermediate. In the text they will be denoted as Oh(f) and Oh(m) respectively. For tetrahedral crystal field the mark will be Td. The theoretic relationships for the magnet moment concerning basically octahedral and tetrahedral crystal fields are subject of the present study.

For the sake of illustration we shall give the exact formula for the magnetic moment of configuration $3d^1$ which corresponds to ions Cr^{5+}, V^{4+}, Mn^{6+}, Ti^{3+}.

$$\mu_{eff} = 8[3x + \exp(-3x/2)]\{x[2 + \exp(-3x/2)]\}^{-1} \qquad (5)$$

where $x = \lambda/kT$

In the second case, the magnetic moment does not depend on temperature and this dependence may be described as follows:

$$\mu_{eff} = f(M^{n+}, CF, \Delta) \qquad (6)$$

To calculate the magnetic susceptibility, B. Bleany and K.D.Bouers [7] deduced the following equation for complex transition metals with different ligands:

$$\chi_{mol} = N_a\mu_B^2 g[3k(t-\theta)^{-1}\{1 + 1/3enp(-2J/kT)\}^{-1}(1-\rho) + Na\mu_B\rho(4kT)^{-1} + \chi_{pol} \qquad (7)$$

where g is a spectroscopic splitting factor, ρ is the relative impurity content, and J is the exchange integral and χ_{pol} - polarization paramagnetism.

Magnetic moments of 3d transition element ions

Titanium may be present in compounds in three oxidation states: Ti(II),Ti(III) and Ti(IV) with electron configuration...d^2,d^1,d^0. Ti(IV) has a negligible magnetic moment and for that reason its compounds are diamagnetic. The magnetic moments of Ti(II) and Ti(III) depend on the oxidation state, and on the type of crystal field and its strength. Figs. 1 and 3 show the dependences on temperature (Fig. 1) and crystal field strength (Fig. 3). Obviously, with oxidation state Ti(III) the magnetic moment strongly depends on temperature, a dif-

ference existing with intermediate and strongly octahedral fields. It can be seen also that the magnetic moment of Ti^{3+} in Oh crystal field depends strongly on temperature as well. It is important that, according to data on magnetic moment values it is possible to determine whether titanium is in 3+ or 2+ oxidation state since the differences between the magnetic moment values are rather large (Fig. 1). In tetrahedral coordination (Td) the titanium ions differ again in magnetic moments.
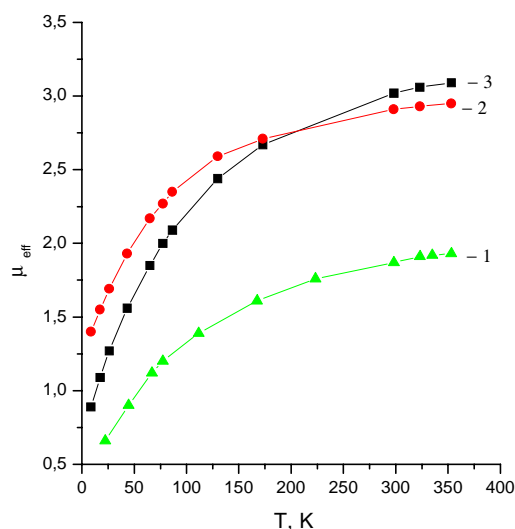

Fig. 1. Dependence of the magnetic moment μ_{eff}(BM) on coordination – octahedral (Oh) and tetrahedral (Td) and temperature T(K) as well for titanium. Curves: 1 - Ti^{3+}, Oh (m) ; 2 - Ti^{2+}, Oh (f) ; 3 - Ti^{2+}, Oh (m).
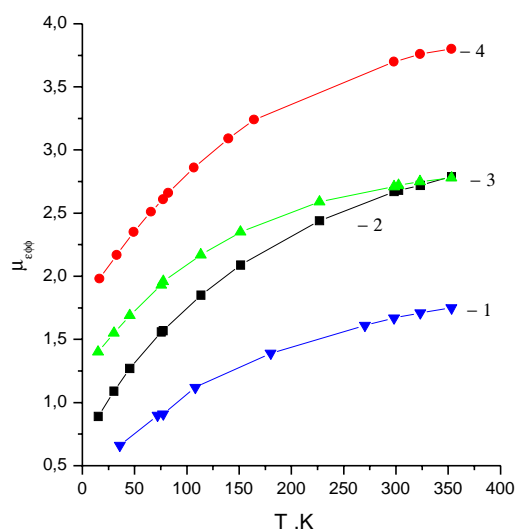

Fig. 2. Dependence of the magnetic moment μ_{eff}(BM) on coordination – octahedral (Oh) and tetrahedral (Td) and temperature T(K) as well for vanadium. Curves: 1 - V^{4+}, Oh (m,f); 2 - V^{3+},Oh(m); 3 - V^{3+}, Oh (f) ; 4 - V^{2+}, Td.
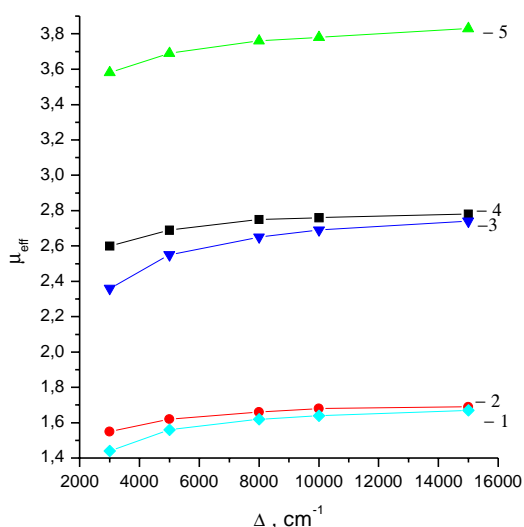
Fig. 3. Dependence of the magnetic moment μ_{eff}(BM) on the coordination, both octahedral (Oh) and tetrahedral (Td), and on the crystal field strength Δ(cm^{-1}) for vanadium. Curves 1- V^{4+}, Td; 2 - Ti^{3+}, Td; 3 - V^{2+}, Td; 4 - V^{5+}, Oh(f).

Fig. 4. Dependence of the magnetic moment μ_{eff}(BM) on coordination – octahedral (Oh) and tetrahedral (Td) and temperature T(K) as well for chromium. Curves: 1 - Cr^{5+}, Oh(m); 2 - Cr^{4+}, Oh(m) ; 3 - Cr^{4+}, Oh(f) ; 4 - Cr^{3+}, Td ; 5 - Cr^{2+}, Oh(f); 6 - Cr^{2+},Td.

It should be noted that here the magnetic moment is independent of temperature. The dependence of the magnetic moment on the crystal field strength is more pronounced with a weak crystal field.

Vanadium has the following four oxidation states: V(II),V(III),V(IV) and V(V) which correspond to electron configurations: 3d^3,3d^2,3d^{1}and 3d^0. In 3d^0 V(V) configuration it does not possess its own magnetic moment and its compounds are diamagnetic. Fig. 2 shows the dependence of the magnetic moments on temperature for three oxidation states of vanadium (V(II),V(III) and V(IV). Evidently, there are significant differences between the magnetic moment values, depending on the oxidation state of the vanadium ion. The highest magnetic moment belongs to V(II) (Td). It is interesting that in Oh field for the magnetic moment μ, this ion is high enough but does not depend on temperature. In Oh field all these ions have different moments, which facilitates their determination with respect to oxidation state and coordination. In a Td field the magnetic moments of V(IV),V(III) and V(II) do not depend on temperature but their differences are sufficient for their identification. On Fig. 3 the relationship between μ_{eff} and the crystal field strength is presented.

In the case of chromium and manganese we have the most complicated picture. Chromium may have the following oxidation states: Cr(VI),Cr(V),Cr(IV),
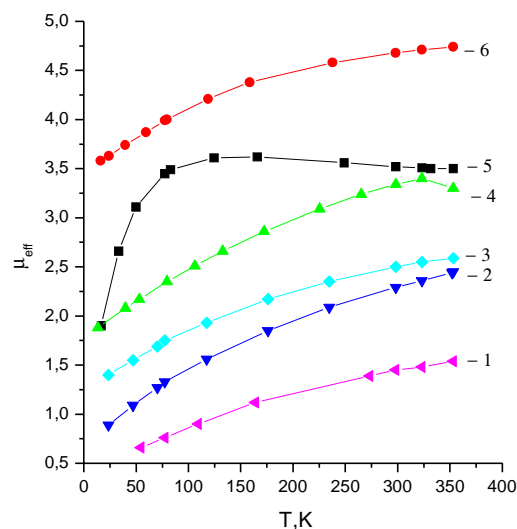
Cr(III), Cr(II) and Cr(I) which correspond to electron configurations 3d^0,3d^1,3d^3, 3d^4 and 3d^5.Similarly to all elements in configuration 3d^0, the magnetic moment is zero and the compounds are diamagnetic. Figs. 4 and 6 present the dependences of the magnetic moment on temperature (Fig. 4) and the strength of the crystal field (Fig. 6). It is seen again that, depending on the oxidation state and the coordination, the magnetic moments are different. With manganese there is the same situation illustrate the magnetic moments of this element depending on temperature (Fig. 5) and the crystal field strength (Fig. 6).

The dependences of the magnetic moments of iron and cobalt in different oxidation states on temperature and crystal field strength are shown in Fig.7. Significant differences in the magnetic moment values depending on the ion state of these elements at different temperatures are observed. It is interesting that at temperatures above 250 K, the magnetic moment shows only a very weak dependence on temperature. As to the crystal field strength, in contrast to the ions of titanium, vanadium, chromium and manganese, the magnetic moment drops with rising crystal field strength (Fig.8). This permits, upon measuring the magnetic moment in different compounds (complexes) where difference in crystal field strength is expected, to estimate, in addition to the crystal field type, also its strength. In a strong Oh field
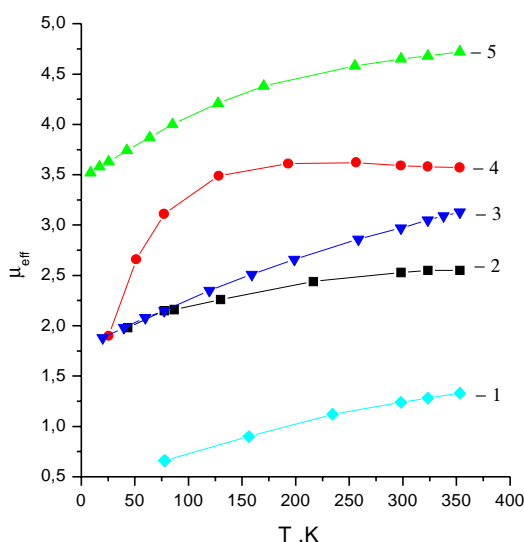
Fig. 5. Dependence of the magnetic moment μ_{eff}(BM) on coordination – octahedral (Oh) and tetrahedral (Td) and temperature T(K) as well for manganese. Curves: 1 – Mn^{6+}, Oh (m, f) ; 2 – Mn^{2+}, Oh (m, f) ; 3 – Mn^{4+},Td ; 5 – Mn^{3+},Td.
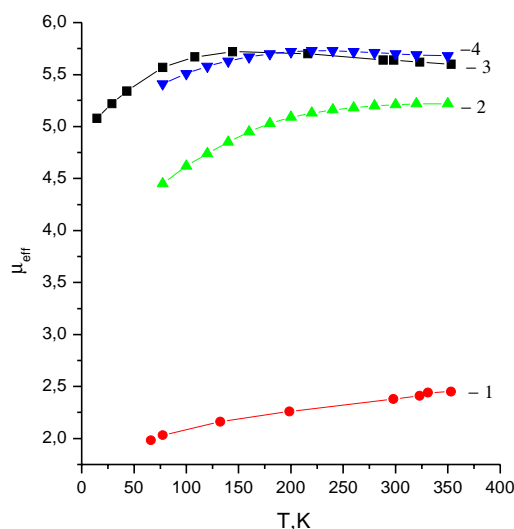

Fig. 7. Dependence of the magnetic moment μ_{eff}(BM) on coordination – octahedral (Oh) and tetrahedral (Td) and temperature T(K) as well for iron and cobalt. Curves: 1 – Fe^{3+},Oh(f) ; 2 – Co^{2+}Oh(m) ; 3 – Fe^{2+}Oh(m) ; 4 – Co^{3+}Oh(m).

Fig. 6. Dependence of the magnetic moment μ_{eff}(BM) on the coordination, both octahedral (Oh) and tetrahedral (Td), and on the crystal field strength Δ(cm^{-1}) for chromium and manganese. Curves: 1 – Mn^{6+},Td ; 2 – Cr^{5+}·Td ; 3 – Cr^{4+}·Oh(m,f); 6 – Mn^{3+}·Oh(m); 7 – Cr^{2+}·Oh(m).
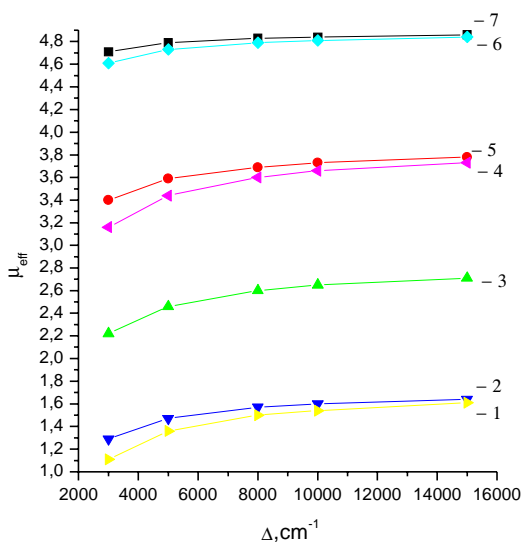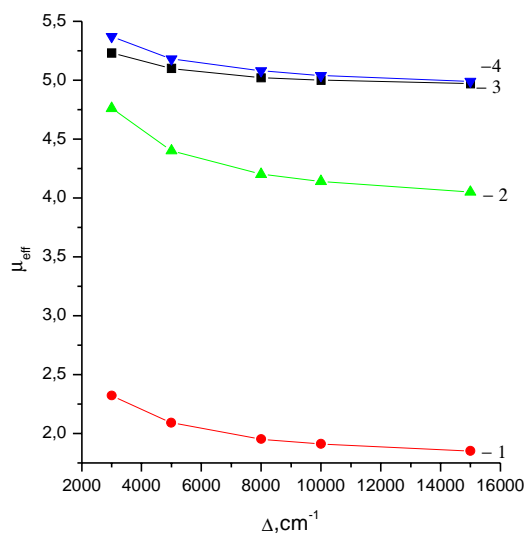

Fig. 8. Dependence of the magnetic moment μ_{eff}(BM) on the coordination, both octahedral (Oh) and tetrahedral (Td), and on the crystal field strength Δ(cm^{-1}) for iron and cobalt. Curves: 1 - Co^{2+}, Oh(f) ; 2 - Co^{2+}, Td ; 3 - Fe^{2+}·Td ; 4 - Co^{3+}, Td.

the magnetic moment of Co(III) is zero. Figs. 9 and 10 present the magnetic moments of nickel and copper ions depending on temperature and crystal field strength. The magnetic moments of Ni(II) and Ni(III) exhibit a significant difference. In the case of the Cu(II) ion (the Cu(I) ion being diamagnetic) the coordination and the strength of the crystal field can be determined.

It is evident that the theoretical dependences of the magnetic moments of 3d transition element ions permit obtaining information on the oxidation state of a given metal center in a given complex, its coordination and interaction with different ligands. These possibilities are widely used and we shall present some examples of our studies on the structure of complexes by magnetic methods.
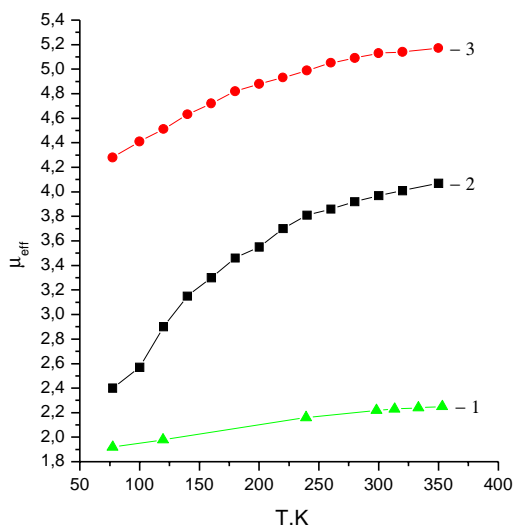
Fig. 9. Dependence of the magnetic moment μ_{eff}(BM) on coordination – octahedral (Oh) and tetrahedral (Td) and temperature T(K) as well for nickel and cuprum. Curves: 1 – Cu^{2+}, Td ; 2 – Ni^{2+}, Td ; 3 – Ni^{3+}, Oh (m).
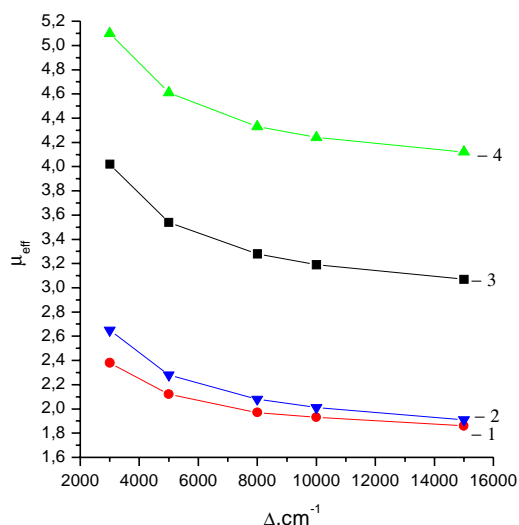
Fig. 10. Dependence of the magnetic moment μ_{eff}(BM) on the coordination, both octahedral (Oh) and tetrahedral (Td), and on the crystal field strength Δ(cm^{-1}) for nickel and cuprum. Curves: 1 - Ni^{3+}·Oh(f) ; 2 - Cu^{2+},Oh (m,f) ; 3 - Ni^{2+}, Oh(m,f) ; 4 – Ni^{3+}, Td.

DISCUSSION

Complexes of copper with a series of organic ligands with different biological activity are often used as drugs and are therefore of special interest. Typical examples of such compounds are complexes with antihypertensive properties, which have been the object of numerous investigations. The presence of several types of donor atoms in them and the possibility for formation of chelate complexes make them very suitable for such studies. One of them is the widely used β-blocker atenolol which binds the Cu(II) ions in a stable complex [8]. In this case the oxidation state of copper in the complex and its coordination are of importance. The study of the magnetic properties of the complex [8] has shown the dependence of the magnetic susceptibility to be a decreasing function of temperature, in the temperature range investigated, the complex being paramagnetic and the oxidation state of the copper, Cu(II). The Curie Weiss law is not followed and, hence, the magnetic moment depends on temperature. The magnetic moments determined for different temperatures coincide with the calculated ones as shown in Fig. 10 and vary in the same way: the magnetic moment increases with temperature. In this way one obtains exact information on the state of copper and the structure of the complex under consideration. The conclusions on the structure were later confirmed also by direct X-ray analysis [8].

During complexation between Cu(II) and the antihypertensive agent oxprenolol [9], formation of mono and binuclear complexes is possible. Magnetic measurements [9] give reliable results on the state of copper during the formation of these complexes. The binuclear complex is antiferromagnetic with T = 323 K, which indicates that here we have an example of coupling of the Cu(II) centers, leading to disappearence of the EPR signal of Cu(II) in the complex. Hence, the complex structure and the position of the copper ions should permit antiferromagnetic interaction between the copper sites. In contrast, the mononuclear complex is paramagnetic and its magnetic moment depends on temperature. This shows that the Cu(II) ions in this case are in tetrahedral coordination, which was proved directly also by X-ray analysis.

The complexes of copper with the antihypertensive drug alprenolol are also of two types: binuclear and mononuclear [10]. Magnetic measurements of these complexes show that in the case of the binuclear ones there is no antiferromagnetic interaction and, similarly to the mononuclear complex, they are paramagnetic. The coordination of Cu(II) is tetrahedral. There is, however a deviation from the theoretical value of the magnetic moment in the case of the mononuclear complex at temperatures above 300 K, which leads to the conclusion that there is deformation of the tetrahedron at

these temperatures, which is also confirmed by X-ray studies [10]. Such a deformation was also established by magnetic measurements on complexes of copper with homocystein [11]. This is a binuclear paramagnetic complex where, however, the Curie Weiss law is not followed and Cu(II) ion is in tetrahedral coordination. Above 300 K there is again a deviation of the experimentally determined magnetic moment from the theoretical. This, as already mentioned, is due to a measurable deformation of this structure above a certain temperature limit. Numerous literature data show that of all compounds under consideration, Cu(II) most often prefers a tetrahedral coordination, although there is a large number of complexes in which this ion is stabilized in an octahedral coordination. This is, e.g. the case of Cu(II) complexes with clenbuterol [12]. Here, depending on the reaction conditions, formation of both binuclear and mononuclear complexes is possible. The dependence of the magnetic susceptibility on temperature is in this case characteristic of the antiferromagnetic state since this quantity shows a maximum at about 80 K. With decreasing the temperature, the magnetic susceptibility begins to increase, which is characteristic of the paramagnetic state. This anomalous shape of the magnetic susceptibility dependence on temperature is attributed either to the presence of magnetic admixtures [13] or, which is more probable, is due to a change in the exchange interaction with the drop of temperature [14]. The binuclear complex is paramagnetic and here the Curie-Weiss law is valid: the magnetic moment does not depend on temperature but only on the crystal field strength. This shows that the coordination of the copper ion is in this case octahedral.

According to the magnetic measurements, the same behavior is characteristic of the mononuclear and binuclear complexes of copper with propaphenone [15]. The mononuclear complex is paramagnetic over the whole temperature range of measurement (2-353 K). The magnetic moment does not depend on temperature, and hence, Cu(II) is in octahedral coordination. In the case of the binuclear complex the temperature dependence of the magnetic susceptibility shows an anomalous shape, similar to that of the copper complex described above [16].

CONCLUSIONS

The present data show that important information can be obtained for a given complex by magnetic measurements. In the first place, the oxidation state of the 3d element participating in the complex is determined, and then its coordination and interaction with the ligand is estimated. The relationships illustrated in the Figures may be used in studies of new complexes of these metals, obtaining information from the temperature dependences of the magnetic susceptibility.

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