

Synthesis, Characterization and Properties of Dinuclear High-spin Five-Coordinate 3d Metal Complexes with NN-bis(2-diethylaminoethyl)-2-hydroxyethylamine

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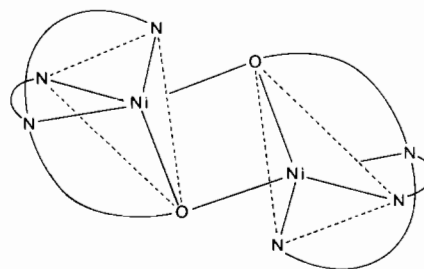
Compounds of general formula $M(\text{bdhe})\text{ClO}_4$ ($M = \text{Mn, Fe, Co, Ni, Cu, Zn}$) are formed by reaction between the tripod-like ligand NN-bis(2-diethylaminoethyl)-2-hydroxyethylamine (bdhe) and metal diperchlorate in acetone. Conductometric, spectroscopic and X-ray diffraction data indicate that all these compounds contain dinuclear high-spin five-coordinate $M_2(\text{bdhe})_2^{2+}$ cations. Variable temperature (80–290 K) magnetic susceptibility data show the existence of a large antiferromagnetic exchange interaction for the copper(II) complex; weak antiferromagnetic interactions have been also observed for the cobalt(II) and nickel(II) derivatives.

Introduction

Although many papers concerning the metal-metal interactions in polynuclear transition metal complexes have been published in recent years [1–7], few reports appeared on series of homologous compounds formed by the same ligand with a large number of metal ions.

The study of these classes of compounds should be, in principle, very useful as, by comparing the magnetic properties of series of isostructural derivative, it could provide information on the role of the electronic properties of the different metal ions in determining the superexchange interactions between the metal ions themselves.

With this in mind we have considered the tripod-like ligand NN-bis(2-diethylaminoethyl)-2-hydroxyethylamine ($\text{Et}_2\text{NCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}$ (bdhe) which is known to form a dimeric $\text{Ni}_2(\text{bdhe})_2(\text{ClO}_4)_2$ derivative [8], in which the hydroxy group of the ligand is deprotonated. An X-ray diffractometric analysis showed that this compound contains five-coordinate dimeric oxygen-bridged $\text{Ni}_2(\text{bdhe})_2^{2+}$ cations, whose geometrical structure can be schematically indicated as follows



This ligand can form an homologous series of perchlorate derivatives with 3d divalent metal ions from manganese(II) to zinc(II). These complexes have been characterized through magnetic, conductometric and spectroscopic measurements, whose results are reported here.

Experimental

Synthesis of the Ligand

2-Hydroxyethylamine (15 g, 0.25 mol) was dissolved in absolute ethanol (250 ml), then powdered potassium carbonate (83 g, 0.6 mol) was added and the resulting mixture was heated at 70 °C. A solution of $\text{Et}_2\text{NCH}_2\text{CH}_2\text{Br}\cdot\text{HBr}$ (130 g, 0.5 mol) in ethanol (350 ml) was added dropwise with stirring during 8 hours, then the mixture was heated under reflux for 24 hours. The solution was filtered and concentrated to a small volume, then mixed with an equal volume of diethyl ether and filtered again. After evaporation of the solvent the residue was fractionally distilled under reduced pressure. The fraction distilling at 112–115°/0.3 Torr was collected, redistilled and stored in desiccator over solid KOH. Found: C, 64.4; H, 12.9; N, 16.0; $\text{C}_{14}\text{H}_{33}\text{N}_3\text{O}$ requires C, 64.81; H, 12.82; N, 16.19%.

Preparation of the Complexes

All the complexes were prepared by the same general method. To a solution of the appropriate

TABLE I. Analytical Data for the $M_2(\text{bdhe})_2(\text{ClO}_4)_2$ Complexes.

Compound	% Found			% Calcd.		
	C	H	N	C	H	N
$\text{Mn}_2(\text{bdhe})_2(\text{ClO}_4)_2$	41.1	8.3	9.8	40.68	7.80	10.16
$\text{Fe}_2(\text{bdhe})_2(\text{ClO}_4)_2$	40.7	7.9	9.8	40.63	7.79	10.15
$\text{Co}_2(\text{bdhe})_2(\text{ClO}_4)_2$	40.4	8.0	10.1	40.34	7.73	10.08
$\text{Ni}_2(\text{bdhe})_2(\text{ClO}_4)_2$	40.4	8.2	10.0	40.36	7.74	10.08
$\text{Cu}_2(\text{bdhe})_2(\text{ClO}_4)_2$	39.6	7.8	10.0	39.89	7.65	9.97
$\text{Zn}_2(\text{bdhe})_2(\text{ClO}_4)_2$	39.5	7.4	9.7	39.77	7.63	9.93

TABLE II. *d* Spacing Values (Å) from X-ray Powder Photographs of $M_2(\text{bdhe})_2(\text{ClO}_4)_2$ Complexes (M = Co, Ni, Cu, Zn).^a

Co	Ni	Cu	Zn
10.10 s	10.10 s	11.11 m	10.10 s
7.42 m	7.42 m	8.55 s	7.42 s
6.19 w	6.20 w	6.55 w	6.22 w
5.96 m	6.02 m	5.72 s	5.99 s
5.55 w	5.57 w	4.96 w	5.57 w
4.96 s	4.98 s	4.66 w	4.96 s
4.30 m	4.30 s	4.30 w	4.30 m
3.87 m	3.93 s	3.74 m	3.91 m
3.68 s	3.70 s	3.31 w	3.68 s
3.41 w	3.40 w	2.94 m	3.41 w
3.09 w	3.05 w	2.53 w	3.09 w
2.86 m	2.86 m	2.16 w	2.86 m
2.76 m	2.74 w		2.76 m
2.70 w	2.70 w		2.70 w
2.58 w	2.53 w		2.55 w
2.31 w	2.33 w		2.33 w
2.13 w	2.13 w		2.14 w

^as = strong, m = medium, w = weak.

metal diperchlorate (2 mmol) in acetone (30 ml), a solution of the ligand (3 mmol) in the same amount of solvent was added. Crystals began to appear after few minutes; they were filtered, washed with acetone and dried *in vacuo*. The use of dry solvent and dry nitrogen atmosphere throughout was essential in the case of manganese(II) and iron(II) derivatives, because of their high sensitivity to oxidation and moisture.

Materials and Physical Measurements

All solvents were reagent grade. Spectrophotometric, magnetic and conductometric measurements were carried out as described previously [9]. Electron paramagnetic resonance spectra were obtained with a Varian E-9 spectrometer, operating at 9 GHz, using diphenylpicrylhydrazone (DDPH) as external standard ($g = 2.0037$).

Results and Discussion

Crystalline compounds of analytical formula $M(\text{bdhe})\text{ClO}_4$ (M = Mn, Fe, Co, Ni, Cu, Zn) have been obtained by reaction of the appropriate metal diperchlorate and an excess of the ligand in acetone. This excess has been found essential since a basic medium is required in order to obtain high yield reaction. The elemental analyses of the obtained compounds are shown in Table I. The manganese(II) and iron(II) derivatives are extremely sensitive to oxygen and to atmospheric moisture and therefore their manipulation must be carried out under dry nitrogen.

The X-ray powder patterns of the cobalt(II) and zinc(II) complexes are practically identical to that of the nickel(II) derivative (see Table II) thus indicating for these compounds a similar structural geometry and therefore the existence of dimeric five-coordinate $M_2(\text{bdhe})_2^{2+}$ cations in the solid state. The X-ray powder pattern of the copper(II) derivative is significantly different. X-ray powder diagrams of the manganese(II) and iron(II) derivatives, although they appear similar to that of the nickel(II) complex, are of poor quality and are not reported in Table II.

The i.r. spectra of all these complexes in the range 4000–250 cm^{-1} are quite superimposable. No absorption band is present in the range 3500–3000 cm^{-1} , where $\nu(\text{O-H})$ stretching is expected, thus supporting the hypothesis of deprotonation of the hydroxy-group of the ligand. The lack of any splitting of the ν_3 and ν_4 (at ca. 1100 and 625 cm^{-1}) active infrared absorption bands is consistent with the presence of uncoordinate perchlorate ion [10].

All the complexes are reasonably soluble in non-hydroxylated polar organic solvents without apparent decomposition. Conductometric dilution studies in acetonitrile show that all the complexes follow the Onsager law, the slope of $\Lambda_o - \Lambda_e$ vs. $c^{1/2}$ plots being in the range of typical uni-divalent electrolytes [11, 12]. The conductance values at 20 °C are reported in Table III.

Electronic spectra in the range 5–25 kK have been recorded both in solid state and in solution. Spectro-

TABLE III. Physical Data for the $M_2(\text{bdhe})_2(\text{ClO}_4)_2$ Complexes.

Compound	Λ_M^a ($\text{cm}^2 \text{ ohm}^{-1}$)	State ^b	Absorption max. (kK) with ϵ_{molar} for soln. in parentheses ^c
$\text{Mn}_2(\text{bdhe})_2(\text{ClO}_4)_2$	286	R	16
$\text{Fe}_2(\text{bdhe})_2(\text{ClO}_4)_2$	291	R	5.5, 7.4sh, 11, 17.3, 19.5, 22.0
		AN	5.1 (19), 10.9 (14)
$\text{Co}_2(\text{bdhe})_2(\text{ClO}_4)_2$	285	R	5.7, 6.4, 13.0, 17.2, 20.8
		AN	5.5 (17), 6.3 (16), 13.0 (17), 17.2 (40), 20.8 (77)
$\text{Ni}_2(\text{bdhe})_2(\text{ClO}_4)_2$	290	R	6.9, 9.4sh, 11.2, 15.4, 20sh, 23.4
		AN	6.8 (15), 11 (22), 12.2 (16), 15.3 (18), 20.4sh, 24 (97)
$\text{Cu}_2(\text{bdhe})_2(\text{ClO}_4)_2$	284	R	10sh, 13
		AN	10sh, 13.5 (184)
$\text{Zn}_2(\text{bdhe})_2(\text{ClO}_4)_2$	293	—	—

^aFor ca. 10^{-3} M soln. in acetonitrile at 20 °C. ^bR = Diffuse Reflectance; AN = Acetonitrile. ^csh = shoulder.

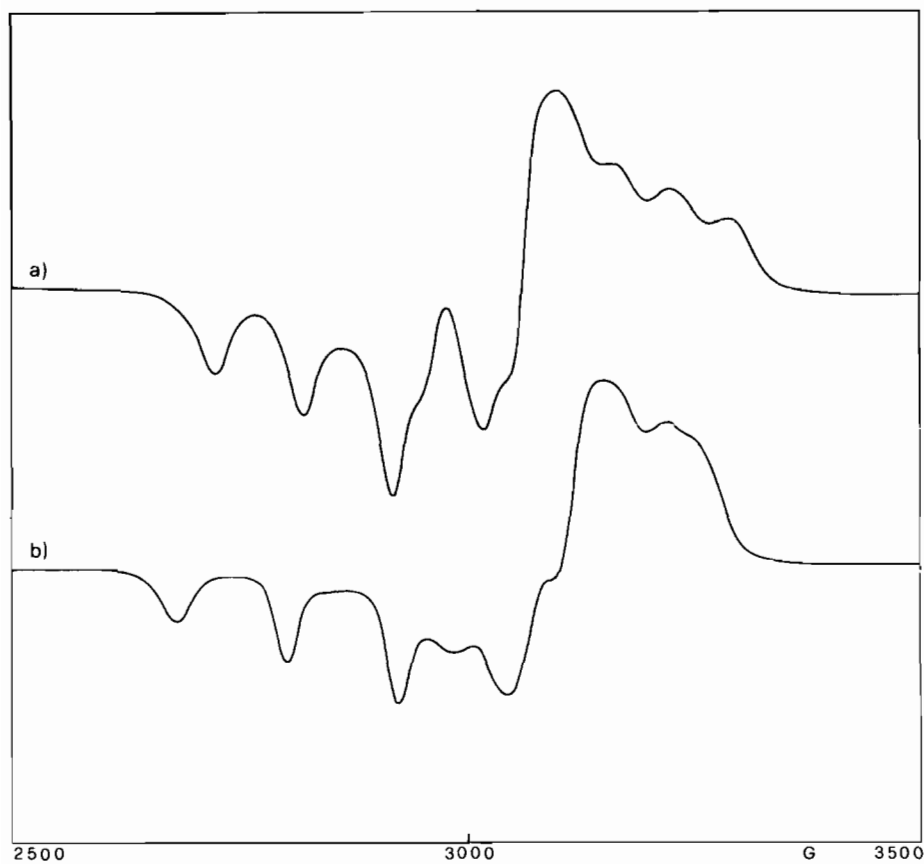


Fig. 1. Polycrystalline powder ESR spectra at 80 K of a) ~1% Cu-doped $\text{Zn}_2(\text{bdhe})_2(\text{ClO}_4)_2$, b) ~1% Zn-doped $\text{Cu}_2(\text{bdhe})_2(\text{ClO}_4)_2$.

photometric data are reported in Table III. The striking similarity for any given metal between the reflectance and absorption ligand field spectra indi-

cates that the structures of the chromophores are probably the same in the solid state and in solution.

The ligand field spectra of the iron(II), cobalt(II) and nickel(II) complexes show the typical features of the high-spin five-coordinate chromophores having a distorted trigonal bipyramidal geometry [13, 14].

Assuming for the three chromophores an idealized C_{3v} symmetry, the following assignment can be performed in order to interpret the observed pattern of absorption bands. The two intense bands at 5.5 kK and 11 kK, which appear in the spectrum of the iron(II) derivative, can be assigned to the spin-allowed transition between the $^5E''$ ground state and the excited $^5E'$ and $^5A_1'$ states, respectively. The weak absorption bands, which appear at high frequencies in the reflectance spectrum, are to be attributed to spin-forbidden transitions involving the quintuplet ground state and excited triplet states [13–15].

The electronic spectra of the cobalt(II) and nickel(II) derivatives are similar to those of the $[Co(Me_6tren)NCS]NCS$ and $[Ni(Me_6tren)NCS]NCS$ complexes, whose spectra have been assigned on the basis of single crystal spectroscopic investigations [16, 17]. According to the results reported in these studies, the following assignments can be suggested for the present cobalt(II) and nickel(II) bdhe complexes. The bands at 5.5 and 6.4 kK, which appear in the reflectance spectrum of the cobalt(II) complex, are to be attributed to electronic transitions involving the 4A_2 ground state and the first 4E excited level, whereas the band at 13 kK is to be attributed to the transition between the 4A_2 and the second 4E term. The bands at higher frequencies, *i.e.* 17.4 and 20.5 kK, are assigned to the $^4A_2 \rightarrow ^4A_2(P)$ and the $^4A_2 \rightarrow ^4E(P)$ transitions, respectively. The spectrum of the nickel(II) complex shows two bands at 6.9 and *ca.* 9 kK, which can be assigned to the $^3E' \rightarrow ^3E''$ transition, and a band at 15 kK, to be attributed to the $^3E' \rightarrow ^3A_2'$ transition; the higher energy absorption at 20.4 and 24 kK are to be assigned to the $^3E' \rightarrow ^3E''(P)$ and $^3E' \rightarrow ^3A_1'(P)$ transitions, respectively.

Preliminary results of single crystal studies on these two derivatives at 4 K support these assignments [18].

The spectrum of the copper(II) complex, which shows a single broad band at 13.5 kK with a shoulder at 10 kK, although not diagnostic, is quite consistent with a five-coordinate trigonal bipyramidal structure of the chromophore [19].

In order to gain new information on the structural geometry of this complex, the ESR spectra of solid samples containing this chromophore have been considered, as both g and A parameters have been shown to be strongly related to the structural geometry of five-coordinate copper(II) complexes [20]. Since, as well be shown below, the present copper(II) derivative is diamagnetic at low temperature, we have prepared a zinc(II)-doped $Cu_2(bdhe)_2(ClO_4)_2$ complex and a copper(II)-doped $Zn_2(bdhe)_2(ClO_4)_2$ complex. As the two solids are not isomorphous, this

allowed us to study the same magnetically diluted $CuZn(bdhe)_2^{2+}$ heterodinuclear system in two different host lattices. The powder ESR spectra of the two solid solutions at liquid nitrogen temperature (Fig. 1) show, with some significant differences, the same general features. It is apparent that in both the compounds the copper(II) chromophore is characterized by a strong rhombic distortion, which, together with large values of the hyperfine coupling constants A , originates a large spread of the resonances in the high field region of the spectra. In the lack of single crystal data, the correct estimation of the spectral parameters is rather difficult. However, as in particular these spectra are compared with those of copper(II)-doped bis(*N*-methylsilylaldiminato)zinc(II) and bis(3-silylaldiminatopropyl)methylamine)zinc(II) compounds, whose single crystal ESR spectra have been recently reported [20], it can be suggested that the observed spectral characteristics are consistent with a distorted five-coordinate trigonal bipyramidal geometry of the copper(II) chromophores.

The observed differences in these ESR spectra reflect different structural properties of the copper(II)–zinc(II) moiety in the two different host lattices. It can be reasonably suggested that this result can be attributed to 'mimicrism' effects due to crystal packing interactions. For the copper(II)-doped $Zn_2(bdhe)_2(ClO_4)_2$ we can propose a coordination geometry similar to that ascertained for the nickel(II) derivative, according to the observed isomorphism between these two compounds; for the zinc(II)-doped $Cu_2(bdhe)_2(ClO_4)_2$ a more distorted trigonal bipyramidal geometry can be suggested because of the apparent larger difference of the hyperfine constants A values. According to the theory [20], this result could be accounted for by a greater value of the Cu–O–Cu angle with consequent greater distortion of the trigonal bipyramidal polyhedron.

As the reported experimental data evidence the dimeric character of all these complexes, variable temperature magnetic susceptibility measurements were carried out in order to detect the existence of magnetic exchange interactions. Experimental magnetic susceptibility data in the range 86–290 K, as well as the effective magnetic moments data for M(II) ions are reported in Table IV. As can be seen, the copper(II) compound exhibits a large antiferromagnetic exchange interaction, the effective magnetic moment for Cu(II) ion varying from 1.12 BM at 291 K to 0.22 BM at 87 K. Antiferromagnetic coupling is apparent also in the nickel(II) and cobalt(II) complexes, the effective magnetic moments decreasing from 3.2 BM to 2.6 BM for nickel(II) and from 4.36 to 3.64 BM for cobalt(II) in the same temperature range. The magnetic moments of the iron(II) and manganese(II) complexes are 5.26 BM and 5.74 BM respectively, and are practically constant in the

TABLE IV. Magnetic Susceptibility Data for the M₂(bdhe)₂-(ClO₄)₂ Complexes.^a

Compound	T (K)	10 ³ χ _M (cgsu mol ⁻¹)	μ _{eff} /M (BM)
Mn ₂ (bdhe) ₂ (ClO ₄) ₂	295	27.88	5.74
	88	89.39	5.61
Fe ₂ (bdhe) ₂ (ClO ₄) ₂	281	24.40	5.26
	86	78.63	5.22
Co ₂ (bdhe) ₂ (ClO ₄) ₂ ^b	291	16.19	4.36
	271	17.34	4.35
	255	18.29	4.34
	240	19.26	4.32
	225	20.30	4.29
	210	21.21	4.24
	199	22.31	4.23
	175	22.78	4.18
	161	26.47	4.14
	149	28.04	4.10
	136	30.30	4.07
	124	32.07	4.00
	114	33.79	3.94
	101	36.64	3.86
	86	38.32	3.64
Ni ₂ (bdhe) ₂ (ClO ₄) ₂ ^b	290	8.73	3.20
	271	9.34	3.20
	260	9.73	3.19
	248	10.10	3.18
	238	10.48	3.17
	227	10.88	3.16
	217	11.30	3.15
	207	11.70	3.12
	195	12.24	3.10
	184	12.87	3.09
	172	13.49	3.06
	160	14.14	3.02
	150	14.83	3.00
	139	15.71	2.97
	129	16.50	2.93
116	17.30	2.84	
106	18.12	2.78	
97	18.73	2.70	
87	19.25	2.60	
Cu ₂ (bdhe) ₂ (ClO ₄) ₂ ^c	291	1.08	1.12
	285	1.05	1.10
	270	0.98	1.03
	258	0.91	0.97
	243	0.83	0.90
	230	0.77	0.85
	217	0.68	0.77
	202	0.59	0.70
	191	0.51	0.63
	179	0.44	0.56
	167	0.37	0.50
	155	0.26	0.40
	143	0.22	0.36
131	0.19	0.31	
120	0.17	0.29	

TABLE IV. (continued)

Compound	T (K)	10 ³ χ _M (cgsu mol ⁻¹)	μ _{eff} /M (BM)
	109	0.13	0.24
	97	0.12	0.22

^aDiamagnetic correction from Tables = -0.486×10^{-3} cgsu mol⁻¹. ^bT.I.P. correction = 0.200×10^{-3} cgsu mol⁻¹. ^cT.I.P. correction = 0.120×10^{-3} cgsu mol⁻¹.

temperature range investigated, thus indicating the existence, if any, of small metal-metal interactions.

The susceptibility data, corrected for diamagnetism and for temperature independent paramagnetism, for the copper(II), nickel(II) and cobalt(II) complexes (see Table IV) have been least-squares fitted to the equation (1), which is valid assuming an isotropic Heisenberg exchange in a given dⁿ-dⁿ dinuclear system characterized by spin S₁ and S₂ [21]:

$$\chi_M = \frac{Ng^2\beta^2}{KT} \cdot \frac{\sum_S \sum_{M_S} (M_S)^2 \exp(-E(S)/KT)}{\sum_S \sum_{M_S} \exp(-E(S)/KT)} \quad (1)$$

where $S = S_1 + S_2$ and $E(S) = -J/2 [S(S+1) - S_1(S_1+1) - S_2(S_2+1)]$ and the other symbols have their usual meaning. This formula is derived from the formula of Van Vleck, when the Zeemann effect for the dⁿ-dⁿ system is considered. The g and J values which minimize the function

$$U = [\sum_i (\chi_{obs} - \chi_{calc}^{(g,J)})^2 / \chi_{obs}^2]^{1/2}$$

are 2.35 and -17 cm⁻¹ for the cobalt(II) derivative, 2.40 and -35 cm⁻¹ for the nickel(II) derivative and 2.13 and -495 cm⁻¹ for the copper(II) one.

The use of the simple equation (1) ignores the effects of orbital degeneracy of the electronic ground level of a given dⁿ metal ion and, therefore, it should be inappropriate for the nickel(II) complex if, as discussed above, it were characterized by a doubly degenerate ³E ground state. Therefore, whereas the model holds for the copper(II) and cobalt(II) derivatives, which are characterized by orbital singlet states, the obtained results for the nickel(II) complex can be considered to be correct only if one assumes that the distortion from the trigonal bipyramidal D_{3h} symmetry is large enough to split the ³E ground term by an energy larger than kT. If this was not true in the present case, the obtained values could, in principle, lead either to overestimating or to underestimating the importance of the antiferromagnetic interaction, as the orbital effects should be partly accommodated in an incorrect estimation of the g parameter.

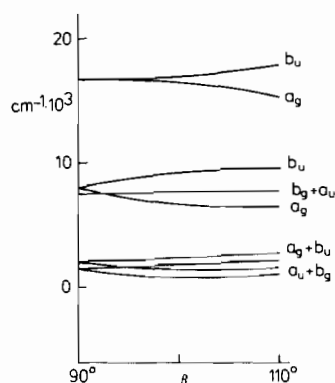


Fig. 2. Energy level diagram for five-coordinate trigonal bipyramidal dimers showing the effect of the variation of the M–X–M angle β (from reference 22).

A qualitative explanation of the magnetic properties observed for these dimeric $M_2(\text{bdhe})_2(\text{ClO}_4)_2$ systems can be given on the basis of an angular overlap model recently proposed by Bencini and Gatteschi [22] in order to interpret the magnetic properties of the copper(II) dimers. Following Hoffmann [23] for a couple of mono-electronic centers (*i.e.* copper(II) ions) the energy difference between the lowest singlet and triplet states is given by

$$E_S - E_T = J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}}$$

where E_S and E_T are the energies of the singlet and the triplet respectively, J and K are coulomb and exchange integrals respectively, a and b are localized molecular orbitals centered on the two different metal ions, ϵ_1 and ϵ_2 are the two highest molecular orbital energies, which can be estimated through the angular overlap model [22]. The energy diagrams which can be obtained from the calculation when the model is applied to five-coordinate trigonal bipyramidal dimers is reported in Fig. 2.

As shown in the diagram, the separation in energy between the a_g and b_u orbitals, which arises from the splitting of d_{z^2} orbitals, strongly depends from the angle M–X–M where M is the metal ion and X is the bridging donor atom. As this angle increases, the difference in orbital energy $\epsilon_1 - \epsilon_2$ increases and therefore an antiferromagnetic coupling between the two metal ions is favoured, the exchange coupling constant J assuming a negative value.

Similar considerations hold for couples of metal ions having more than an unpaired electron, although the calculation is significantly more complicated. However if one qualitatively assumes for cobalt(II) and nickel(II) ions the same energy level diagrams valid for a couple of mono-electronic ions, it can be

observed that several electronic configurations characterized by similar energies can exist. In fact, in both cases unpaired electrons can occupy a_g and b_u orbitals, which originate from the splitting of the two d_{yz} orbitals in this symmetry, or the b_g and a_u deriving from the two d_{xz} orbitals, which in the diagram are characterized by an intermediate energy. As this latter level is doubly degenerate, it can be occupied by two electrons having parallel spins, thus giving a ferromagnetic contribution to the exchange coupling constant J . The resulting ferromagnetic and antiferromagnetic contributions partially cancel each other and a small value of J is observed.

Finally it is worth noting that on the basis of the energy level diagram the M–X–M angle in the copper(II) complex should be significantly greater than that of 103° observed for the nickel(II) complex [10]. This result, which could be supported also by the above ESR data, is probably due to the antiferromagnetic exchange interaction which would stabilize a more distorted coordination geometry.

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