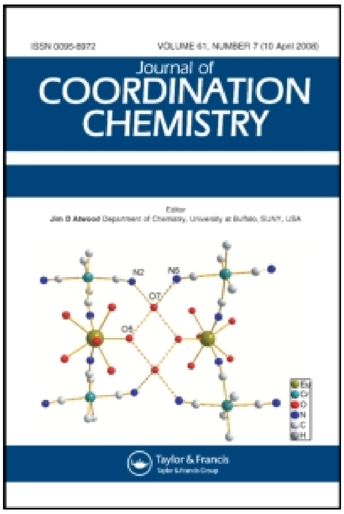

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

EFFECT OF COORDINATED BASE ON MAGNETIC BEHAVIOR OF COPPER(II) CARBOXYLATES WITH FATTY ACID CHAINS (AN ESR STUDY)

M. Valko[a]; M. Mazúr[a]; H. Morris[b]; R. Klement[a]; C. J. Williams[b]; M. Melník[c]
[a] Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Bratislava, Slovakia [b] School of Pharmacy and Chemistry, Liverpool John Moores University, Liverpool, United Kingdom [c] Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, Bratislava, Slovakia

To cite this Article Valko, M. , Mazúr, M. , Morris, H. , Klement, R. , Williams, C. J. and Melník, M.(2000) 'EFFECT OF COORDINATED BASE ON MAGNETIC BEHAVIOR OF COPPER(II) CARBOXYLATES WITH FATTY ACID CHAINS (AN ESR STUDY)', Journal of Coordination Chemistry, 52: 2, 129 — 138

To link to this Article: DOI: 10.1080/00958970008022581

URL: http://dx.doi.org/10.1080/00958970008022581

J. Coord. Chem., 2000, Vol. 52, pp. 129–138
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

EFFECT OF COORDINATED BASE ON MAGNETIC BEHAVIOR OF COPPER(II) CARBOXYLATES WITH FATTY ACID CHAINS (AN ESR STUDY)*

M. VALKO[a,†], M. MAZÚR[a], H. MORRIS[b], R. KLEMENT[a],
C. J. WILLIAMS[b] and M. MELNÍK[c]

[a]*Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovakia;* [b]*School of Pharmacy and Chemistry, Liverpool John Moores University, Byrom Street, Liverpool L3 3AF, United Kingdom;* [c]*Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovakia*

(Received 26 October 1999; In final form 15 February 2000)

The ESR spectra of a series of copper(II) alkanoates with the empirical formula Cu_2X_4 (X = heptanoate, octanoate, nonanoate, decanoate, dodecanoate), and their pyridine adducts have been measured over the temperature range 300 K to 100 K. The spectra of non-adduct copper(II) alkanoates exhibit extreme temperature dependent behavior; the room temperature spectra show a single broad line centered on $g \approx 2.1$, however as the temperature is lowered triplet state features appear. The corresponding pyridine adducts give typical triplet state spectra at all temperatures. This temperature behavior can be interpreted in terms of interdimer interactions in copper(II) alkanoates having the polymeric structure. The observed resonance lines are used to calculate the zero- field splitting parameters D and E. The spin Hamiltonian and zero- field splitting parameters are used to estimate the exchange parameter J. The values of $|2J|$ for the compounds investigated are in the range of 300–400 cm^{-1} and suggest that the copper(II) ions are strongly antiferromagnetically coupled.

---

* The preliminary part of this work was presented at the XV International Conference "Current Trends in Coordination Chemistry", June, 1995, Smolenice, Slovakia.

[†] Corresponding author. Tel.: 421 7 59 325 750, Fax: +421-7-524 93 198, e-mail: mvalko@cvt.stuba.sk

Keywords: Copper carboxylates; ESR; Effect of coordinated base; Binuclear complexes; Fatty acids; Interdimer interaction

INTRODUCTION

Magnetic interactions of copper(II) carboxylates and associated compounds have drawn much interest over the past 45 years and consequently a great deal of experimental and theoretical work has been done [1]. This work has shown that complexes of the general formula $Cu_2(RCOO)_4$ and their adducts, $[Cu(RCOO)_2 \cdot L]_2$, are antiferromagnetic in nature and spin coupling between the unpaired electrons of copper(II) ions operates predominantly by a superexchange interaction *via* the bridging carboxylate ligand. It has also been found, that the magnetic behavior correlates with pK_a values of the parent carboxylic acids or polarizability of the R group, and donor strength of the axial ligand L.

Although many dimeric copper(II) carboxylates have been studied [2] employing spectroscopic, magnetic and X-ray crystallographic techniques, investigations on copper(II) complexes with higher carboxylic acids apart from propionates and butyrates are far less common. Recently, increased interest in copper(II) compounds exhibiting thermotropic columnar mesophases [3] have stimulated studies of binuclear copper(II) alkanoates with $n=6$ to $n=22$, n being equal to the number of carbon atoms of the corresponding fatty acid. However, the main emphasis has been on the thermal behavior of such compounds [4] and therefore we directed our interest to their magnetic properties. In the present paper we report the temperature dependent X-band ESR study of copper(II) carboxylates with fatty acid chains, tetrakis(μ-alkanoato-O,O′) dicopper(II), as well as their pyridine adducts, tetrakis(μ-alkanoato-O,O′) bis(pyridine) dicopper(II) (Fig. 1).

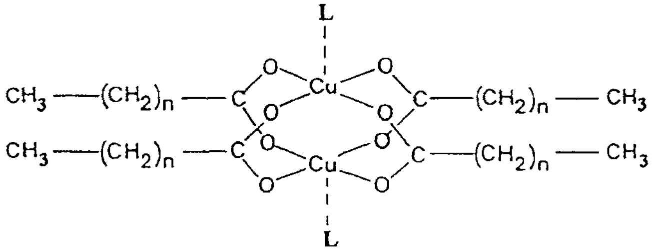

FIGURE 1 A schematic view of the molecular structure of binuclear copper(II) alkanoate.

EXPERIMENTAL

Materials

The fatty acids (heptanoic, octanoic, nonanoic, decanoic and dodecanoic) and copper(II) sulfate were purchase from Fluka Chemica. All chemicals were reagent grade with $> 98\%$ purity.

Synthesis

Copper(II) – heptanoate,-octanoate,-nonanoate,-decanoate and dodecanoate complexes were synthesised by the direct metathesis of the corresponding sodium soap (0.01 mol) in a slightly acidic aqueous solution with the required amount of copper sulfate (0.005 mol) solution, as described previously [2a]. The crude copper soaps were purified by recrystallization from boiling methanol with overall yields of 80 – 90%.

The green products of the type $Cu_2X_4(py)_2$ (X = heptanoate, octanoate, nonanoate, decanoate and dodecanoate; py = pyridine) were prepared by heating pyridine (0.02 mol) with copper(II) carboxylate (0.01 mol) in hot acetone. The mixture was stirred, filtered and left at room temperature. The green crystals were collected by filtration and dried at room temperature. *Anal.* Calc. for ($C_{28}H_{52}O_8Cu_2$): Cu, 19.7; C, 52.2; H, 8.1. Found: Cu, 19.6; C, 52.1; H, 8.1%. *Anal.* Calc. for ($C_{32}H_{60}O_8Cu_2$): Cu, 18.2; C, 54.9; H, 8.6. Found: Cu, 18.3; C, 55.1; H, 8.4%. *Anal.* Calc. for ($C_{36}H_{68}O_8Cu_2$): Cu, 16.8; C, 57.2; H, 9.1. Found: Cu, 16.7; C, 56.0; H, 8.8%. *Anal.* Calc. for ($C_{40}H_{76}O_8Cu_2$): Cu, 15.6; C, 59.2; H, 9.4. Found: Cu, 15.7; C, 59.8; H, 9.1%. *Anal.* Calc. for ($C_{48}H_{92}O_8Cu_2$): Cu, 13.7; C, 62.4; H, 10.0. Found: Cu, 13.4; C, 62.4; H, 9.8%. *Anal.* Calc. for ($C_{38}H_{62}N_2O_8Cu_2$): Cu, 15.8; C, 56.9; H, 7.7; N, 3.5. Found: Cu, 15.5; C, 55.5; H, 7.6; N, 3.5%. *Anal.* Calc. for ($C_{42}H_{70}N_2O_8Cu_2$): Cu, 14.8; C, 58.8; H, 8.2; N, 3.2. Found: Cu, 15.0; C, 58.1; H, 8.2; N, 3.3%. *Anal.* Calc. for ($C_{46}H_{78}N_2O_8Cu_2$): Cu, 13.9; C, 60.4; H, 8.6; N, 3.0. Found: Cu, 13.3; C, 59.6; H, 8.4; N, 3.0%. *Anal.* Calc. for ($C_{50}H_{86}N_2O_8Cu_2$): Cu, 13.1; C, 61.9; H, 8.9; N, 2.9. Found: Cu, 13.4; C, 61.8; H, 9.0; N, 3.0%. *Anal.* Calc. for ($C_{58}H_{102}N_2O_8Cu_2$): Cu, 11.7; C, 64.4; H, 9.5; N, 2.6. Found: Cu, 11.2; C, 64.4; H, 9.5; N, 2.7%.

ESR Measurements

ESR spectra were recorded using a Bruker SRC 200 D spectrometer operating at X-band with a modulation of 100 kHz over the temperature range 100 – 300 K. Low temperatures were reached by using the Bruker variable temperature unit.

RESULTS AND DISCUSSION

The ESR spectra of the copper(II) heptanoate and its pyridine adduct in the temperature range 100 – 295 K are presented in Figures 2 and 3, respectively. Spectra of the other copper(II) alkanoates and their adducts are similar to those presented and show features corresponding to dimeric copper(II) carboxylates [5]. These spectra are governed by the usual $S = 1$ spin

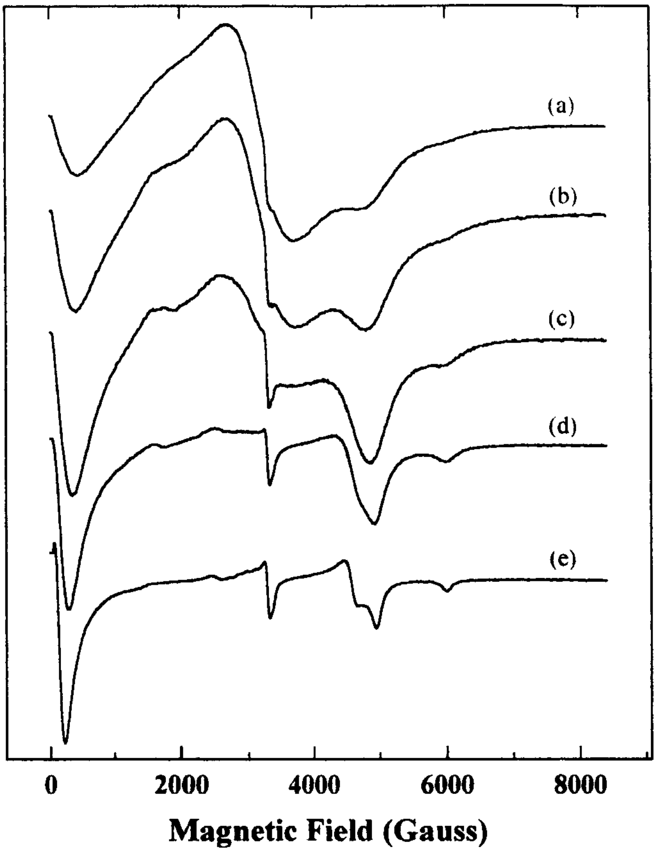

FIGURE 2 The ESR spectra of the copper(II) heptanoate taken at various temperatures: (a) 295 K; (b) 250 K; (c) 200 K; (d) 150; (e) 100 K.

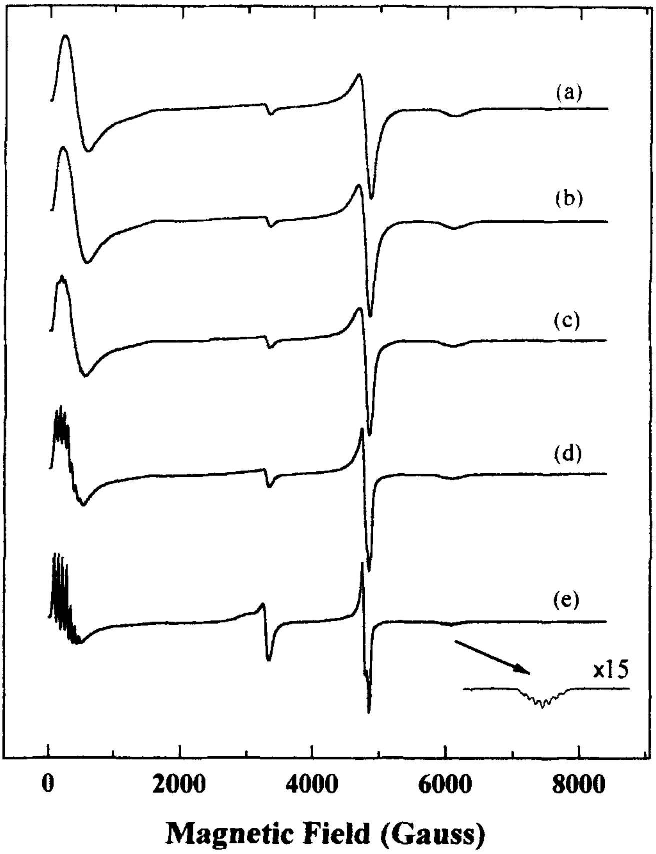

FIGURE 3 The ESR spectra of the pyridine adduct of copper(II) heptanoate taken at various temperatures: (a) 295 K; (b) 250 K; (c) 200 K; (d) 150 K; (e) 100 K.

Hamiltonian [6]

$$\hat{H} = \beta\bar{B} \cdot \bar{\bar{g}} \cdot \hat{S} + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E(\hat{S}_x^2 - \hat{S}_y^2) \tag{1}$$

where D and E are the zero-field splitting parameters; x, y, and z are a principal axis coordinate system fixed with respect to the Cu—Cu bond, and the other symbols have their usual meaning [6]. When the external magnetic field is along, respectively, the x, y and z direction; solution of the spin Hamiltonian (1), in the bases of triplet wave function – pure states [7], yields six allowed ($\Delta m_s = 1$) ESR transitions at resonance fields given by [8]

$$
\begin{aligned}
B_{x1}^2 &= (g_e/g_x)^2[(B_0 - D' + E)(B_0 + 2E')],\\
B_{x2}^2 &= (g_e/g_x)^2[(B_0 + D' - E)(B_0 - 2E')]\\
B_{y1}^2 &= (g_e/g_y)^2[(B_0 - D' - E)(B_0 - 2E')],\\
B_{y2}^2 &= (g_e/g_y)^2[(B_0 + D' + E)(B_0 + 2E')]\\
B_{z1}^2 &= (g_e/g_z)^2[(B_0 - D')^2 - E'^2)],\\
B_{z2}^2 &= (g_e/g_z)^2[(B_0 + D')^2 - E'^2)]
\end{aligned}
\tag{2}
$$

where $B_0 = h\nu/\beta g_e$, $D' = D/\beta g_e$ and $E' = E/\beta g_e$; g_e is the free electron g value. For example, B_{x1} and B_{x2} are the two $\Delta m_s = 1$ resonance fields when the magnetic field is along the x direction. In powders it is, of course, impossible to align the magnetic field along a given direction and the observed spectrum is a sum over all possible orientations. It has been shown [8], however, that sharp discontinuities in the absorption curve occur at just the values of the magnetic field given by Eq. (2) so that even in powders, the axial resonance fields may be obtained and from them we may calculate g_x, g_y, g_z, D and E. It is also known from the angular dependence of the field position and transition probability for dimers, that for $D < 1/2$ hv, the contribution to the spectra from the forbidden $\Delta m_s = 2$ transition is not negligible [9, 10]. Because the forbidden transition is quite isotropic, only one line will appear in the powder spectra. If $D > 1/2$ hv, which is the case of copper carboxylate dimers measured at X-band frequency, the contribution of the forbidden transition to the spectra can be neglected, and then the lines at the resonance fields B_{x1} and B_{y1} and the $\Delta m_s = 2$ line can no longer be observed and the powder spectrum will consist of only four lines. Moreover, if $E = 0$ the number of lines observable is reduced to three.

The room temperature ESR spectra of non-adduct copper alkanoates (Fig. 2) as well as spectra taken above 200 K show extremely broad absorption bands *centered on g* ≈ 2.1 with an indication of lines typical of the dimeric unit ($B_{z1}, B_{\perp 2}, B_{z2}$). As the temperature is lowered below 200 K, the triplet state features at about 200, 4800 and 6100 G emerge. At 100 K, the spectra consist of four lines corresponding to B_{z1}, B_{x2}, B_{y2} and B_{z2} transitions. Similar behavior to this was also observed for other copper carboxylates [11], *e.g.*, copper *n*-butyrate monohydrate.

In contrast to Cu_2X_4 complexes, the pyridine adducts (Fig. 3) at room temperature show very well resolved triplet state spectra. The spectra of copper heptanoate, octanoate, nonanoate and decanoate exhibit three transitions at the resonance fields B_{z1}, $B_{\perp 2}$ ($B_{x2} = B_{y2}$) and B_{z2}; the spectrum of copper dodecanoate consists of all four lines ($B_{x2} \neq B_{y2}$). As the temperature is lowered, the line corresponding at room temperature to $B_{\perp 2}$, is split into two lines (B_{x2}, B_{y2}) which shows that $|E|$ is small but non-zero. This splitting is more significant at lower temperatures and is due to the lack of axial symmetry in the system which causes g_x and g_y to be different, and also introduces the zero-field splitting term $E(\hat{S}_x^2 - \hat{S}_y^2)$ into the spin Hamiltonian (1). From the low temperature spectra it can also be clearly seen that, in all cases, the low-field part of the spectrum exhibits additional lines, a septet with a hyperfine splitting of 65 G, which is due to the interaction of the unpaired electrons with two equivalent copper nuclei ($I = 3/2$) within the dimer unit. In addition, for the heptanoate, decanoate and dodecanoate complexes, the high- field, B_{z2}, transition also shows seven lines. The ESR spectra of all compounds investigated show resonances at positions expected for mononuclear copper(II) species with the spin Hamiltonian parameters: $g_{\parallel} \approx 2.3$, $g_{\perp} \approx 2.04$ and $A_{\parallel} \approx 135$ G; $A_{\parallel}$(mononuclear) $\approx 2A_{z1,z2}$(binuclear) [12]. However, these parameters do not enable us to decide what form the mononuclear impurity takes since it could be a monomeric copper carboxylate complex or adsorbed copper(II) ions, although it has been observed that in zinc-doped binuclear copper(II) systems the non interacting copper(II) ions have almost identical g-values to those of the interacting species [1h, 3]. The spin Hamiltonian parameters (D, E and g values) for dimeric species were determined by an iterative procedure [14] using Eq. (2) and they are summarized in Table I.

Bleaney and Bowers [1a], and Ross and Yates [15] showed that, when isotropic exchange interaction is comparable in magnitude with the spin-orbit coupling, the zero-field splitting parameter D involves the sum of terms arising from the exchange (D_{ex}, *pseudo*-dipolar term) and the dipole–dipole (D_{dd} dipolar term) interactions, and is given by

$$D = D_{\text{ex}} + D_{\text{dd}} = -\frac{1}{8}J\left[\frac{1}{4}(g_{\parallel} - 2)^2 - (g_{\perp} - 2)^2\right] - \left(g_{\parallel}^2 + \frac{1}{2}g_{\perp}^2\right)\frac{\beta^2}{r^3} \quad (3)$$

Since exchange coupling between the copper(II) centers is antiferromagnetic, the exchange parameter J is negative (as defined). This parameter is a measure of exchange interaction; $|2J|$ value is the energy of the singlet – triplet separation. The zero-field splitting parameter, D, determined from experimental spectra was assumed to be positive on the basis of Eq. (3), the distance between metal ions, r, was taken as 2.60 Å for non adduct copper alkanoates and 2.65 Å for their pyridine adducts [16, 17]. The values of the

TABLE I ESR data for the copper(II) alkanoates and their pyridine adducts (*A* = heptanoate, *B* = octanoate, *C* = nonanoate, *D* = decanoate, *E* = dodecanoate)

	Temp./K	$g_\perp$	$g_\parallel$	A_{z1}	A_{z2}	$\lvert D\rvert$	$\lvert E\rvert$	$-J$
				Gauss		cm^{-1}		
						alkanoate complexes		
A	100	2.015	2.292	–	–	0.332	0.010	161
B	100	2.024	2.294	–	–	0.333	0.009	161
C	100	2.012	2.290	–	–	0.331	0.010	161
D	100	2.017	2.288	–	–	0.331	0.010	165
E	100	2.022	2.299	–	–	0.331	0.010	154
						pyridine adducts		
A	295	2.071	2.299	–	–	0.347	–	200
	100	2.060	2.307	62	65	0.347	0.003	173
B	295	2.070	2.308	–	–	0.347	–	185
	100	2.072	2.327	65	–	0.347	–	162
C	295	2.043	2.288	–	–	0.353	–	187
	100	2.039	2.300	65	–	0.352	–	167
D	295	2.069	2.306	–	–	0.347	–	187
	100	2.080	2.321	65	65	0.345	0.005	179
E	295	2.051	2.284	–	–	0.346	0.005	196
	100	2.073	2.310	65	65	0.346	0.006	186

exchange parameters, calculated from Eq. (3) are summarized in Table I. The $-2J$ values of the compound investigated are in the range of values (200–500 cm^{-1}) found for dimeric copper(II) carboxylates and their adducts and suggest that the copper(II) ions are strongly antiferromagnetically coupled. The values estimated for pyridine adducts are somewhat higher than those for non-adduct alkanoates. This effect has been attributed to the donor molecule [1d, 18] (pyridine), which has a tendency to donate electron density to the central copper(II) atom. The electron transfer reduces the positive charge on copper ions, consequently any repulsions between them and also allows the metal 3*d* orbitals to expand giving better overlap.

As was shown on Figures 2 and 3, the non-adduct copper alkanoates, in contrast to their pyridine adducts, exhibit a marked temperature dependence in the ESR spectra. We note, that similar to previous studies [11a] the effect of chain length in respect to the magnetic properties of copper alkanoates appears to be negligible. The temperature dependent behavior of ESR spectra could be interpreted in terms of interdimer interactions. From the crystallographic data it is known, that in anhydrous complexes the carboxylate-bridged dimers are linked into one-dimensional polymeric chains by apical Cu—O interactions of length ~3.0 Å [16]. As a consequence of the polymeric structure of these complexes, the excited triplet states undergo a mutual exchange interaction (intermolecular exchange); the probability for intermolecular exchange to occur is dependent on the concentration of the molecules in the thermally populated triplet state. Due to this type of interaction, the triplet states are delocalized and the triplet excitons exhibit the ability to migrate through the crystal lattice. As was shown by Yablokov *et al.* [19], intermolecular exchange interaction, which results in migration and interaction (collision) of triplet excitons, or more precisely the exchange frequency, is strongly temperature dependent and leads to broadening of the spectra at higher temperatures. Indeed, as the paramagnetic triplet state becomes more depopulated with decreasing temperature this interaction reduces exponentially; so that, at low temperatures, the spectra are similar to those originating from separated molecules in the triplet state. In the case of pyridine adducts, where the interdimer distance is ~9 Å or more [17], the dimeric molecules are sufficiently well separated that intermolecular exchange does not take place and consequently the ESR spectra at room temperature are well resolved and show the typical triplet state features.

Acknowledgements

Sponsorship of this work by the Slovak Grant Agency and The Royal Society (to M.V.) is gratefully acknowledged. The cooperation between Bratislava and Liverpool supported by the British Council, Bratislava is gratefully acknowledged.

References

[1] (a) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* **A214**, 451 (1952); (b) B. N. Figgis and R. L. Martin, *J. Chem. Soc. A*, p. 3837 (1956); (c) M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.* **64**, 99 (1964); (d) R. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc. Dalton*, p. 428 (1972); (e) P. D. Loth, P. Cassoux, J. P. Daudey and J. P. Malrieu, *J. Am. Chem. Soc.* **103**, 4007 (1981); (f) R. D. Harcourt, F. L. Skrezenek and R. G. A. R. Maclagan, *J. Am. Chem. Soc.* **108**, 5403 (1986); (g) A. Bencini and D. Gatteschi, *EPR of Exchange Coupled Systems*, Springer Verlag, Berlin (1990); (h) G. F. Kokoszka, M. Linzer and G. Gordon, *Inorg. Chem.* **7**, 1730 (1968); (i) G. F. Kokoszka and R. W. Duerst, *Coord. Chem. Rev.* **5**, 209 (1970); (j) J. A. Moreland and R. J. Doedens, *Inorg. Chem.* **17**, 674 (1978); (k) G. Plesch, M. Blahová, J. Kratsmár-Šmogrovič and C. Friebel, *Inorg. Chimica. Acta* **136**, 117 (1987); (l) G. Plesch, C. Friebel, O. Švajlenová, J. Kratsmár-Šmogrovič and D. Mlynarčík, *Inorg. Chimica. Acta* **129**, 81 (1987); (m) G. Plesch, C. Friebel, O. Švajlenová, J. Kratsmár-Šmogrovič and D. Mlynarčík, *Inorg. Chimica. Acta* **151**, 139 (1988); (n) G. Plesch, O. Švajlenová, J. Kratsmár-Šmogrovič and M. Kohútová, *Chem. Zvesti* **37**, 169 (1983); (o) J. Sokolík, B. Lučanská, G. Plesch, I. Tumová, A., Valent, P. Švec and J. Kratsmár-Šmogrovič, *Coll. Czech. Chem. Commun.* **58**, 1363 (1993); (p) J. Líška, L'. Danihel, J. Porubský and D. Zeljenková, *Rheumatologia* **8**, 213 (1994); (q) J. Líška, L'. Danihel, J. Porubský and D. Zeljenková, *Rheumatologia* **8**, 190 (1995); (r) J. Líška, J. Porubský, D. Zeljenková, M. Ružičková and E. Surmíková, *Rheumatologia* **8**, 163 (1994).

[2] (a) R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, London (1983); (b) M. Melnik, *Coord. Chem. Rev.* **36**, 1 (1981); (c) M. Melnik, *Coord. Chem. Rev.* **47**, 239 (1982); (d) M. Kato and Y. Muto, *Coord. Chem. Rev.* **92**, 45 (1988); (e) Y. Saito, *Inter. Rev. Phys. Chem.* **8**, 235 (1989); (f) J. Catteric and P. Thorton, *Adv. Inorg. Chem. Radiochem.* **20**, 291 (1977).

[3] (a) A. M. Godquin-Giroud, J. C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Lett.* **45**, L-681 (1984); (b) P. Maldivi, A. M. Godquin-Giroud, J. C. Marchon, D. Guillon and A. Skoulios, *Physica B* **158**, 234 (1989).

[4] (a) H. Abied, D. Guillon, A. Skoulios, P. Weber, A. M. Godquin-Giroud and J. C. Marchon, *Liq. Cryst.* **2**, 269 (1987); (b) H. D. Burrows and H. A. Ellis, *Thermochim. Acta* **52**, 121 (1982).

[5] (a) D. M. L. Goodgame, Y. Nishida and R. E. Winpenny, *Bull. Chem. Soc. Japan* **59**, 344 (1986); (b) M. Valko, M. Melnik, H. Morris, R. F. Bilton and P. Pelikan, *Chem. Phys. Lett.* **183**, 372 (1991); (c) J. Lewis, F. E. Mabbs, L. K. Royston and W. R. Smail, *J. Chem. Soc. A*, 291 (1969); (d) J. R. Wasson, C. Shyr and C. Trapp, *Inorg. Chem.* **7**, 469 (1968).

[6] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clareton Press, Oxford (1970).

[7] The triplet wave functions are not in general pure states, so that this manner of labeling the transitions is somewhat deceptive; however, we follow the usual practice here.

[8] E. Wasserman, L. C. Snyder and W. A. Yager, *J. Chem. Phys.* **41**, 1763 (1964).

[9] (a) J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava and T. D. Smith, *J. Chem. Soc. A*, p. 94 (1969); (b) J. H. Price, J. R. Pilbrow, K. S. Murray and T. D. Smith, *J. Chem. Soc. A*, p. 968 (1970).

[10] T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.* **13**, 173 (1974).

[11] (a) P. Scharrock and M. Melnik, *J. Coord. Chem.* **14**, 65 (1985); (b) J. Mrozinski and E. Heyduk, *J. Coord. Chem.* **13**, 291 (1984); (c) F. Cariati, L. Erre, G. Micera, L. Menabue, M. Saladini and P. Prampolini, *Inorg. Chim. Acta* **63**, 85 (1982); (d) Yu. V. Yablokov and A. V. Ablov, *Doklady Akad. Nauk S.S.S.R.* **144**, 173 (1962).

[12] C. P. Slichter, *Phys. Rev.* **99**, 479 (1955).

[13] G. F. Kokoszka, H. C. Alen and G. Gordon, *J. Chem. Phys.* **42**, 3693 (1965); **46**, 3013 (1967); **47**, 10 (1967).

[14] N. D. Chasteen, *Inorg. Chem.* **10**, 2339 (1971).

[15] (a) I. G. Ross, *Trans. Faraday Soc.* **55**, 1057 (1959); (b) I. G. Ross and J. Yates, *Trans. Faraday Soc.* **55**, 1064 (1959).

[16] (a) T. R. Lomer and K. Perera, *Acta Cryst.* **B30**, 2912 (1974); (b) T. R. Lomer and K. Perera, *Acta Cryst.* **B30**, 2913 (1974); (c) N. Ghermani, C. Lecomte, C. Rapin, P. Steinmetz, J. Steinmetz and B. Malaman, *Acta Cryst.* **B50**, 157 (1994).

[17] M. Petric, I. Leban and P. Šegedin, *Polyhedron* **12**, 1973 (1993).

[18] (a) W. E. Marsh, G. O. Carlisle and M. V. Hanson, *J. Mol. Struc.* **40**, 153 (1977); (b) W. E. Marsh, G. O. Carlisle and M. V. Hanson, *J. Inorg. Nucl. Chem.* **39**, 1839 (1977); (c) J. Lewis, Y. C. Lin, L. K. Royston and R. B. Thompson, *J. Chem. Soc.* p. 6464 (1965).

[19] (a) V. V. Gavrilov, Yu. V. Yablokov, L. N. Milkova and A. V. Ablov, *Phys. Stat. Sol.* **B45**, 603 (1971); (b) L. V. Mosina and Yu. V. Yablokov, *Phys. Stat. Sol.* **B62**, K51 (1974).