

Some solid effects in iron(II) complexes with ligands of potential biological interest

Juan Costamagna, Luis Araya, Ramón Latorre

Departamento de Química, Facultad de Ciencia, Universidad de Santiago
and Departamento de Química, Facultad de Ciencias, Universidad de
Chile, Casilla 653, Santiago, Chile.

Abstract - New complexes of iron(II) with bidentate ligands derived from 5-bromo-salicylaldehyde and monosubstituted anilines have been synthesized and characterized by chemical analyses and conventional spectroscopies. Several properties were characterized in these complexes in the solid phase: (a) absence of oxygen bridges, (b) anomalously high magnetic moment values at room temperature, (c) an antiferromagnetic behavior at low temperatures, (d) a doublet Mössbauer spectrum with a normal isomer shift value for low spin iron(II) complexes at room temperature, (e) presence of hyperfine pattern Mössbauer spectra at 4K with at least a sextuplet and a doublet having an internal magnetic field of ca 460 KOe. These results together with the simulation curves of magnetic susceptibilities versus temperature, suggest the existence of at least two sites for the iron atom and could tentatively be interpreted assuming the existence of a formal planar geometry around the iron atoms, probably in a triplet state, and ferrimagnetic-antiferromagnetic interactions.

INTRODUCTION

A great deal of information on properties of synthetic ligands of potential biological interest have been arising during the last years (ref. 1). Among them, several Schiff bases were characterized and employed as models for a series of systems (ref. 2); the relevant role which they play in contemporary coordination chemistry has recently been emphasized (ref. 3). Also, non-hemo and non-sulphur complexes of iron(II) (and iron(III)) were used as models for a better understanding of some metalloproteins such as oxyhemerittrines (ref. 4) and dioxygenases (ref. 5). Some Schiff bases are considered suitable ligands for these latter systems.

On the other hand, the attainment of ferromagnetic products at room temperature has required quite a strong endeavor (ref. 6) since, with the exception of the synthesis of ferrites, there has been a limited experimental success; also, the theoretical advance in this subject has been rather slow (ref. 7). In addition, almost exclusively antiferromagnetic properties at room temperature has been found in some binary compounds comprising first transition series elements and coordination compounds with organic ligands (ref. 8); moreover, certain ferro or ferrimagnetic properties of these type of compounds were not found (refs. 8,9).

In some iron(II) complexes with ligands derived from Schiff bases which create a N_2O_2 or N_2S_2 environment around the metallic atom, the existence of antiferromagnetism (ref. 10) together with the crossing of spectroscopic terms of different multiplicities (ref. 11) has been informed. Additionally, some of these complexes show dimeric antiferromagnetic structures due to irreversible oxidations by molecular oxygen (ref. 12). In the present work, the synthesis, characterization and some solid effects observed in iron(II) complexes with bidentate Schiff bases derived from 5-bromo salicylaldehyde (5BrSA) and mono substituted anilines (Y Anil), shown in Fig. 1, are presented and discussed.

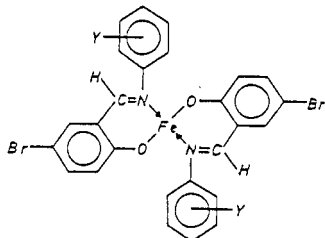


Fig. 1. Iron(II) complexes;
Y : 2-Cl, 3-Cl, 4-Cl, 2-CH₃,
3-CH₃, 4-CH₃ or H.

EXPERIMENTAL

Infrared spectra in nujol mull or KBr, were recorded with a Perkin-Elmer 621 spectrophotometer in the range 4000-400 cm^{-1} .

The Mössbauer spectra of these complexes, as fine powder samples, were obtained in a conventional spectrometer with constant acceleration. The source was 10 mCi ^{57}Co in a Pd matrix. The gamma rays detection was carried out with a Reutes-Stokel detector connected to an Ortec amplifying and selecting system. A 1024 channel Canberra multichannel analyzer was used for the acquisition of information. The low temperature determinations were conducted in a liquid Helium experimental container. The reported isomer shift values are relative to sodium nitroprusside.

Magnetic susceptibilities measurements between 4-300 K were performed using the Superconducting Quantum Interference Device-Varian method at 5.0 KOe; those measurements in the range 150-400 K, were carried out using the Faraday method employing a Cahn 7600-RTL balance at 5.0 KOe.

C, H, N, Cl and Br microanalyses were performed in Laboratorio de Microanálisis, Universidad de Buenos Aires, Argentine and Mikroanalischen Labor Paschen, RFA. Iron was determined and characterized by complexometry. The syntheses and characterization of the ligands was reported previously (ref. 13).

Synthesis of the complexes. 2.25 mmol of the ligand was dissolved in acetone and the pH was adjusted to 6.5-7 by addition of sodium hydroxide. To the resulting solution, 1.125 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in water, was added and the mixture was stirred for 2 hours, keeping a constant pH value. The solid was filtered out, washed with acetone-water and dried in vacuo over phosphorous pentoxide.

The melting point of the complexes derived from chloroaniline lie above 255 $^\circ\text{C}$, while those derived from methylaniline are in the range 87-175 $^\circ\text{C}$. The complexes are brown colored except for the $[\text{Fe}(\text{5BrSA-2CH}_3\text{Anil})_2]$ which is yellow.

Analysis: $\text{C}_{26}\text{H}_{22}\text{O}_2\text{N}_2\text{Br}_2\text{Fe}$. Calculated: C, 53.03; H, 3.50; N, 4.42; Br, 25.20; Fe, 8.81, %; found: $[\text{Fe}(\text{5BrSA-4CH}_3\text{Anil})_2]$, C, 50.50; H, 3.70; N, 4.69; Br, 25.40; Fe, 8.85; $[\text{Fe}(\text{5BrSA-3CH}_3\text{Anil})_2]$, C, 52.00; H, 3.34; N, 4.62; Br, 24.90; Fe, 8.83; $[\text{Fe}(\text{5BrSA-2CH}_3\text{Anil})_2]$, C, 51.80; H, 3.90; N, 4.71; Br, 26.10; Fe, 8.80.

$\text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_2\text{Br}_2\text{Cl}_2\text{Fe}$. Calculated: C, 46.26; H, 2.39; N, 4.15; Br, 23.67; Cl, 10.52; Fe, 8.27, %; found: $[\text{Fe}(\text{5BrSA-4ClAnil})_2]$, C, 43.80; H, 2.52; N, 4.20; Br, 22.50; Cl, 9.80; Fe, 8.20; $[\text{Fe}(\text{5BrSA-3ClAnil})_2]$, C, 44.50; H, 2.62; N, 3.90; Br, 23.20; Cl, 9.81; Fe, 8.20; $[\text{Fe}(\text{5BrSA-2ClAnil})_2]$, C, 44.20, H, 2.38, N, 4.40; Br, 22.67; Cl, 9.94; Fe, 8.25.

RESULTS AND DISCUSSION

The infrared spectra of the complexes show few, but significant changes compared to those of the free ligands, in the regions of $\mu\text{-N}$ and $\mu\text{-O}$, together with the absence of the wide and strong $\mu\text{-OH}$ band located ca. 3000 cm^{-1} . Furthermore, no new bands were detected in the regions of 1100 and 800 cm^{-1} , thus indicating the absence of superperoxide or peroxide in these complexes (ref. 14).

The values of isomer shifts and quadrupolar splitting at room temperature for the complexes are summarized in Table I (ref 15). The observed isomer shifts and quadrupole splitting values are similar to those reported by Goldanskii *et al* for iron(II) complexes with analogous ligands (ref. 16). From these results, it can be tentatively assumed a planar symmetry, with the iron(II) in a low spin state, with a $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} = d_{yz}$ energy orbital d levels and the likely occurrence of a triplet state due to the proximity of d_{xy} and d_{z^2} orbitals (ref. 17). $[\text{Fe}(\text{phtalocyanine})]$ is one of the few examples of pseudo-planar complexes of iron(II); however, in this compound the isomer shift is 2.62 and the quadrupole splitting is 0.65 mm/s at -110 $^\circ\text{C}$ (ref. 18).

On the other hand, it can be seen that isomer shift values are slightly affected by the substituents on the aniline ring: according to Fluck (ref. 19) the degree of covalence should increase in the order $\text{Cl} > \text{H} > \text{CH}_3$. This fact is only observed when the substituent is in the para position in aniline. Retrodonation effects, which may compensate metal-ligand donation effects, would probably cause no remarkable differences in those values.

Table 1 also show magnetic moment values at different temperatures. Figure 2 shows the effect of substituents on the magnetic moments of the complexes at room temperature. It can be seen that these values are higher than those reported for iron(II) Schiff bases complexes, 4.9-5.1 Bohr magnetons (ref. 18, ref. 20), suggesting the existence of ferromagnetic interactions in the solid phase.

TABLE 1. Mössbauer data at room temperature and magnetic moments at different temperatures

Compounds	MOSSBAUER DATA ^a		MAGNETIC MOMENTS ^b		
	δ	ΔE_Q	298 K	MAXIMUM	6 K
[Fe(5BrSA-Anil) ₂]	0.41	0.74	10.37	11.76(180)	2.99
[Fe(5BrSA-2ClAnil) ₂]	0.40	0.77	10.56	17.84(180)	3.48
[Fe(5BrSA-3ClAnil) ₂]	0.41	0.88	9.73	12.78(140)	2.30
[Fe(5BrSA-4ClAnil) ₂]	0.43	0.77	8.02	10.20(220)	1.97
[Fe(5BrSA-2CH ₃ Anil) ₂]	0.41	0.68	6.09	6.48(189)	1.79
[Fe(5BrSA-3CH ₃ Anil) ₂]	0.41	0.72	6.87	-	-
[Fe(5BrSA-4CH ₃ Anil) ₂]	0.38	0.75	11.70	12.08(200)	2.78

^a δ , isomer shift; ΔE_Q , quadrupole splitting; in mm/s, relative to sodium nitroprusside.

^b in Bohr magnetons; the temperature of the maximum magnetic moment is pointed out in parenthesis.

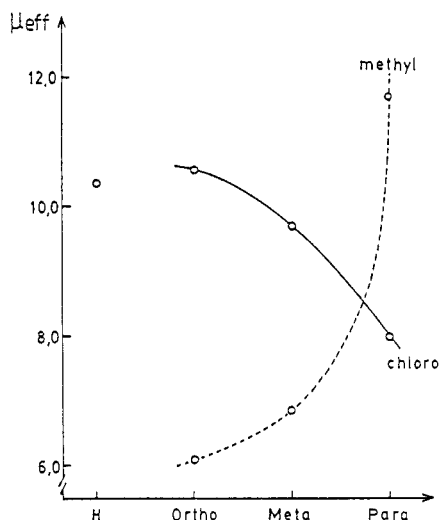


Fig. 2. Room temperature magnetic moments, μ_{eff} , in Bohr magnetons for [Fe(5BrSA-YAnil)₂] complexes; Y: H, ortho-, meta-, para-methyl or chloro.

Anomalously high values for magnetic moments were reported for ferrites and similar inorganic compounds (refs. 6,7). Moreover, some complexes of iron(II), such as [Fe(pyridine)₂(SCN)₂], [Fe(2,2'-dipyridine)₂Cl₂], [Fe(5,5'-dimethyl-2,2'-dipyridine)₂Cl₂] (ref. 21) showed a ferromagnetic behavior at low temperature.

Table 1 also includes the maximum magnetic moments and their corresponding temperatures, which are below 220 K for all the complexes (ref 15). Also, the magnetic moments at 6K are pointed out. These values suggest antiferromagnetic interactions.

The relatively high magnetic moments observed for these complexes in the solid state disappear in chloroform solutions where they show a magnetic moment of 3.3-3.5 Bohr magnetons.

Mössbauer spectra and magnetic susceptibilities at low temperatures

Results of magnetochemistry are difficult to reconcile with those from Mössbauer spectroscopy at room temperature. Figure 3 shows the Mössbauer spectra at different temperatures for [Fe(5BrSA-4ClAnil)₂] and [Fe(5BrSA-Anil)₂]. The presence of a hyperfine interaction, with six splitted lines and a isomer shift identical to that obtained at room temperature, is observed. These facts confirm the existence of ferromagnetic interactions and suggest the presence of at least two sites for the iron atoms, each one having the same electronic density. The [Fe(5BrSA-4ClAnil)₂] Mössbauer spectra at different temperatures have been shown because, in addition to the twelve lines observed for all the complexes, a doublet with the same room temperature isomer shift but with a quadrupole splitting, of ca. 0.77 mm/s is noteworthy.

Some internal magnetic field values, obtained from the external lines of the hyperfine spectra (ref. 22) and measured in KOe are: [Fe(5BrSA-Anil)₂], 465; [Fe(5BrSA-2ClAnil)₂], 474; [Fe(5BrSA-4CH₃-Anil)₂], 465. These values lie between those of metallic iron

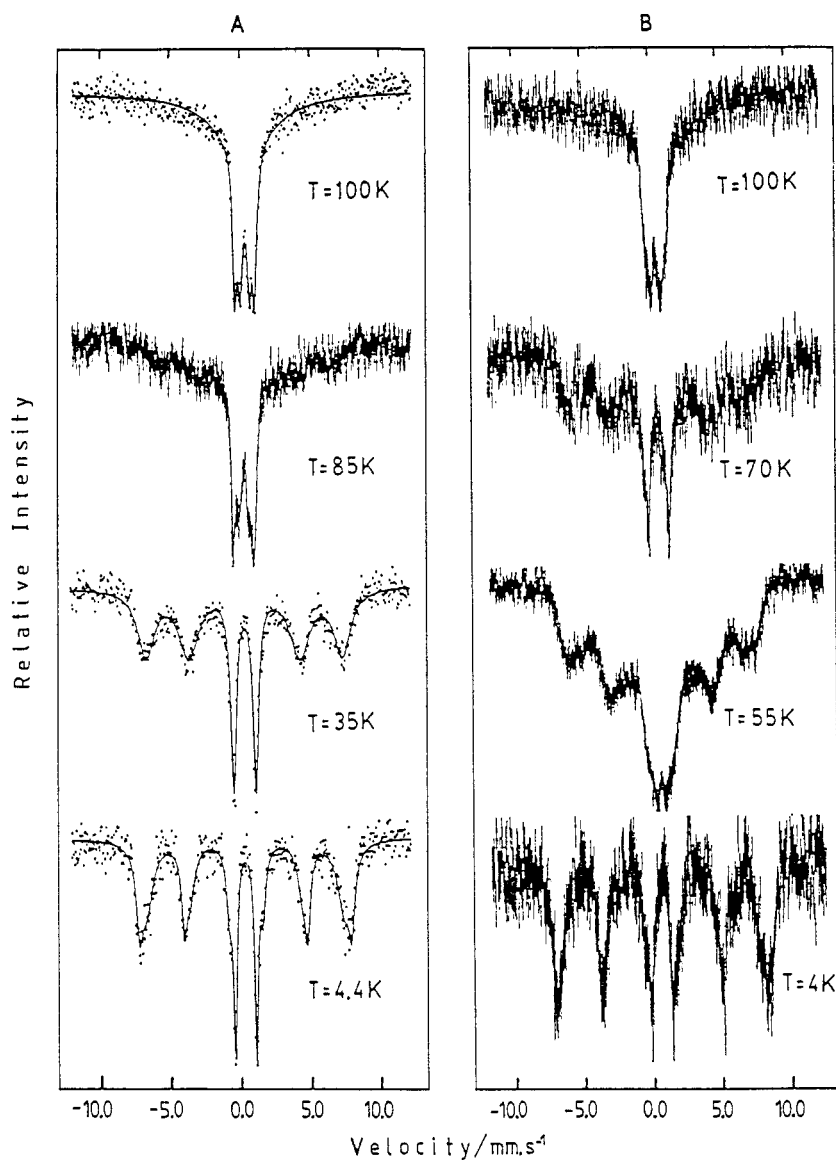


Fig. 3. Mössbauer Spectra at low temperatures :
 A, $[\text{Fe}(\text{5BrSA-4ClAnil})_2]$; B, $[\text{Fe}(\text{5BrSA-Anil})_2]$

(330 K Oe) and α -ferrite, $\alpha\text{-Fe}_2\text{O}_3$ (517 K Oe) (ref. 22) and confirm the ferromagnetic interactions observed for these complexes.

The Mössbauer results obtained at low temperatures suggest that the apparent contradiction between Mössbauer and magnetic susceptibilities could be explained in terms of the existence of relaxation phenomena with temperature dependence (ref. 23). Thus, the existence of two lines at 300 K can be interpreted as an average value with a relaxation time smaller than 10^{-7} s which is the half time life of ^{57}Fe (ref. 24).

Figure 4 shows the variation of the molar magnetic susceptibility with temperature in the range of 3 to 360 K for three of the complexes studied: $[\text{Fe}(\text{5BrSA-2ClAnil})_2]$, $[\text{Fe}(\text{5BrSA-4ClAnil})_2]$ and $[\text{Fe}(\text{5BrSA-Anil})_2]$. The experimental data suggest that it would be possible that the complexes have a ferrimagnetic behaviour, rather than a ferromagnetic one, at some temperature, followed by antiferromagnetism at lower temperatures. In some complexes an additional "residual paramagnetism" like is observed at low temperatures.

The proposed ferrimagnetic phenomenon is supported by the Mössbauer results, shown in Fig. 3, which suggest the existence of at least two sites for the iron atoms (*vide supra*).

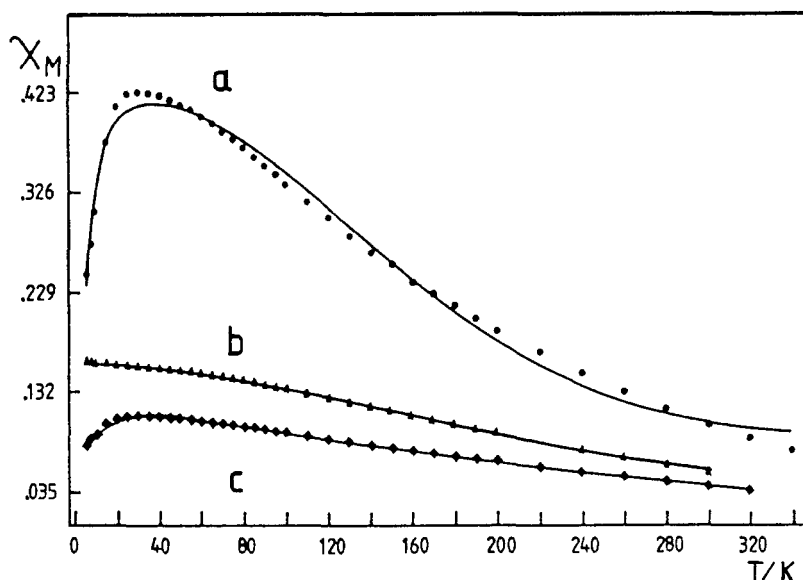


Fig. 4. Molar magnetic susceptibilities, χ_M , in the range 4-360 K and simulation curves for: $[\text{Fe}(\text{5BrSA-2ClAnil})_2]$ (a), $[\text{Fe}(\text{5BrSA-4CH}_3\text{Anil})_2]$ (b) and $[\text{Fe}(\text{5BrSA-4ClAnil})_2]$ (c).

The data shown in the Fig. 4 do not fit any of the previous known treatments (ref. 25) and they could only be reasonably adjusted for all the complexes throughout the equation (1), except for $[\text{Fe}(\text{5BrSA-4ClAnil})_2]$ which follows the equation (2):

$$\chi_M = c_1 \exp(-k^2T^2/j_1.j_2) + c_2 / (k^2T^2 + c_3) + c_4 (kT)^{1/2} \quad (1)$$

$$\chi_M = c_1 \exp(-k^2T^2/j_1.j_2) + c_2 kT / (k^2T^2 + c_3) \quad (2)$$

where k is the Boltzman constant in cm^{-1} , $j_1.j_2$ are the coupling constants related to the ferrimagnetic exchange interactions, and c_1 to c_4 are adjustable parameters.

The first term in both equations could physically be related to that ferrimagnetism. The second and third terms (only the second in equation (2)) would take into account the "residual paramagnetism" and the antiferromagnetic behaviour; it was not possible to find mathematical formulations which separate both phenomena. The solid lines shown in the Fig. 4 belong to the calculated values through equations (1) or (2) (Note a).

Table 2 shows the parameters obtained from the equations (1) and (2) and the extrapolated values of molar magnetic susceptibilities at 0 K. From these results, it is possible to outline some remarks. $[\text{Fe}(\text{5BrSA-4ClAnil})_2]$ shows the greater apparent ferrimagnetic nature. Also, there is no a clear relationship between the kind (and place) of the substituents and the magnetic properties. On the other hand, only $[\text{Fe}(\text{5BrSA-2ClAnil})_2]$ shows a negative c_2 parameter, in agreement with the strong antiferromagnetic character observed at low temperatures. In addition, the extrapolated values of the molar magnetic

TABLE 2. Magnetic parameters from equations (1) and (2) and molar magnetic susceptibility, χ_M , at 0 K

Compounds	$(j_1.j_2)^{1/2}$ (cm^{-1})	c_1	c_2	c_3	$c_4 \cdot 10^3$	χ_M (0 K)
$[\text{Fe}(\text{5BrSA-Anil})_2]$	137	0.153	31.4	1550	2.18	0.173
$[\text{Fe}(\text{5BrSA-2ClAnil})_2]$	124	0.467	-7.2	21	5.26	0.070
$[\text{Fe}(\text{5BrSA-3ClAnil})_2]$	106	0.252	30.0	1580	3.42	0.266
$[\text{Fe}(\text{5BrSA-4ClAnil})_2]$	206	0.071	1.9	627	-	0.073
$[\text{Fe}(\text{5BrSA-2CH}_3\text{Anil})_2]$	130	0.049	5.7	357	0.79	0.065
$[\text{Fe}(\text{5BrSA-4CH}_3\text{Anil})_2]$	162	0.138	16.5	1010	1.94	0.155

Note a: The parameters c_1 - c_4 and the coupling constant j_1 and j_2 were adjusted using a special non linear regression program. Detailed data could be sent upon request to R.L.

susceptibilities at 0 K is different from zero in all the complexes studied. Surprisingly, $[\text{Fe}(\text{5BrSA-3ClAnil})_2]$, which apparently has the lower exchange interactions, is the compound which shows the greatest molar magnetic susceptibility at 0 K.

For the sake of comparison, iron(III) complexes with a composition $\text{Fe}(\text{5BrSA-YAnil})_2\text{Cl}$ in solid phase have recently been synthesized (ref 26). Ionic monomeric planar species have been detected in non aqueous solvents. Preliminary results show that they are dimeric in solid phase with no oxygen bridges (ref. 27); having a normal magnetic moment at room temperature for a high spin iron(III) species and a typical antiferromagnetic behaviour at low temperatures (ref 28). Mössbauer spectra interpretation is in progress.

Acknowledgements

The authors acknowledge R.O.Frankel(MIT) for equipment facilities and PNUD/UNESCO (CHI 84/006), Fondo Nacional de Ciencia y Tecnología (no. 1115/88), Departamento Técnico de Investigación, Universidad de Chile (no. Q20028744) and Dirección de Investigaciones Científicas y Tecnológicas, Universidad de Santiago (no. 16-03-8432CM) for financial support.

REFERENCES

- (a) E.Bayer, E.Koch and G.Anderegg, *Angew.Chem.Int.Ed.Engl.*, **26**, 545 (1987); (b) Y.Tor, J.Libman, A.Shanzer and S.Lifson, *J.Am.Chem.Soc.*, **109**, 6517 (1987).
- R.W.Hay, in D.R.Williams (Ed.), *An Introduction to Bio-Inorganic Chemistry*, Chapter 4, Charles C.Thomas, New York (1976).
- (a) D.E.Fenton, *Proc.Int.Conf.Coord.Chem.*, **23**, 132 (1984); (b) M.I.Terekhova, Yu.N.Belokon', V.I.Maleev, N.I.Chernoglazova, K.A.Kochetkov, V.M.Belikov and E.S.Petrov, *Isv.Akad.Nauk.SSSR.Ser.Khim.*, 905 (1986).
- M.Y.Okamura and I.M.Klotz, in G.I.Eichhorn (Ed.), *Inorganic Biochemistry*, p. 320, Elsevier, New York (1973).
- J.W.Pyrz, A.L.Roe, L.J.Stern and L.Que, *J.Am.Chem.Soc.*, **107**, 614 (1985).
- B.D.Cullity, *Introduction to Magnetic Materials*, Chapters 4&5, Elsevier, New York (1984).
- J.L.Smock, *New Developments in Ferromagnetism*, Chapter 4, Elsevier, New York (1980).
- R.Parthenet, *Ann.Phys.*, **17**, 5 (1982).
- Y.Maeda, S.Shite, Y.Takashima, Y.Nishida, *Bull.Chem.Soc.Japan*, **50**, 2902 (1977).
- P.J.Marini, K.S.Murray, B.O.West, *J.Chem.Soc.Dalton*, 143 (1983).
- (a) P.J.Marini, K.J.Berry, K.S.Murray, B.O.West, *J.Chem.Soc.Dalton*, 879 (1983); (b) H.J.Pignolet, G.S.Patterson, J.F.Weiber, R.H.Holm, *Inorg.Chem.*, **13**, 1263 (1974).
- M.D.Hobday, T.D.Smith, *Coord.Chem.Rev.*, **9**, 311 (1972).
- L.Araya, J.Vargas and J.Costamagna, *Transition Met.Chem.*, **11**, 319 (1986).
- L.Vaska, *Acc.Chem.Res.*, **9**, 175 (1976).
- L.Araya, R.Latorre and J.Costamagna, *Proc.Int.Conf.Coord.Chem.*, **23**, 136 (1984); **24**, 279 (1986).
- (a) R.A.Stukan, V.I.Goldanskii, E.F.Makarov, E.G.Rukhadze, *Zhur.Struct.Khim.*, **8**, 239 (1967); (b) Y.Tashima and T.Tateishi, *Bull.Chem.Soc.Japan*, **38**, 1688 (1965).
- E.König, G.Rotter and H.A.Goodwin, *Inorg.Chem.*, **20**, 3677 (1981).
- E.Fluck, in V.I.Goldanskii and R.H.Herber (Eds.), *Chemical Applications of Mössbauer Spectroscopy*, p. 279, Academic Press, New York (1968).
- W.Kerler, W.Neuwirth, E.Fluck, P.Kuhn and B.Zimmermann, *Z.Physik*, **173**, 321 (1963).
- W.Fitzsimmons, A.W.Smith, L.F.Larkvorty and K.A.Rogen, *J.Chem.Soc.Dalton*, 676 (1977).
- (a) W.M.Reiff, R.B.Frankel, B.F.Little and G.J.Long, *Inorg.Chem.*, **13**, 9 (1974); (b) W.M.Reiff, D.Dookum, M.A.Weber and R.B.Frankel, *Inorg.Chem.*, **14**, 4 (1975).
- J.Danon in V.I.Goldanskii and R.H.Herber (Eds.), *Chemical Applications of Mössbauer Spectroscopy*, Chapter 3, Academic Press, New York, (1968).
- (a) P.Gutlich, R.Link and A.Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, p. 97, Springer Verlag, New York (1978); (b) A.Vértés, L.Korecz and K.Buerger, *Mössbauer Spectroscopy*, p. 46, Elsevier, New York (1979).
- G.R.Hoy in G.J.Long (Ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Chapter 8, Plenum Press, New York (1984).
- (a) W.Wojciechowski, *Inorg.Chim.Acta*, **1**, 319 (1967); (b) D.C.Mattis, *The Theory of Magnetism*, Springer-Verlag, New York (1981).
- J.Costamagna, R.Latorre, J.Vargas and L.Araya, unpublished results.
- K.S.Murray, *Coord.Chem.Rev.*, **12**, 1 (1974).
- L.Borer, L.Thalken, C.Cecarelli, M.Glick, J.H.Zhang and W.M.Reiff, *Inorg.Chem.*, **22**, 1719 (1983).