Inorganica Chimica Acta, *192* (1992) 107–115

The heterodinuclear iron(III) and copper(II) molecule Cu(salen)Fe(acac)$_2$NO$_3$ and its iron precursor Fe(acac)$_2$NO$_3$. Synthesis, magnetic susceptibility, EPR and Mössbauer investigations*

Daniel Laroque**, Irène Morgenstern-Badarau†
Laboratoire de Chimie Bioorganique et Bioinorganique, URA 1384, Université Paris-Sud XI, Bâtiment 420, 91405 Orsay (France)

Heiner Winkler, Eckhard Bill, Alfred X. Trautwein†
Institut für Physik, Medizinische Universität zu Lübeck, 2400 Lübeck (FRG)

and Miguel Julve
Department de Quimica Inorgànica, Facultat de Ciències Quimiques de la Universitat de València, 46100 Burjassot, Valencia (Spain)

(Received September 2, 1991; revised October 15, 1991)

Abstract

The synthesis, EPR, magnetic and Mössbauer properties of two iron(III) complexes are reported. The heterodinuclear iron(III)–copper(II) complex Cu(salen)Fe(acac)$_2$NO$_3$ is obtained as an adduct from the reaction of the two mononuclear moieties, the Cu(salen) molecule and the mononuclear iron(III) molecule Fe(acac)$_2$NO$_3$ acting as a precursor of the dinuclear unit. The latter molecule itself has been prepared by ligand substitution from the tris-acetylacetonate Fe(acac)$_3$. The dinuclear complex is characterized by comparing the properties of the mono- and the dinuclear complex. Fe(acac)$_2$NO$_3$ is identified from its typical IR spectrum with the main nitrate vibrations at 1380, 1250 and 1010 cm^{-1} and an axial $S=5/2$ EPR spectrum in the solid state. Ligand rearrangement occurs in solution as indicated by the presence of only ionic nitrate and a rhombic EPR spectrum. The dinuclear molecule presents a very modified IR spectrum, where the copper(salen) phenolic oxygen vibration and the bound-nitrate vibrations have disappeared; additionally no EPR spectrum can be recorded at X-band frequency. The magnetic data have been interpreted using spin-Hamiltonian formalism. From magnetic susceptibility measurements, in the solid state, the following set of parameters has been determined: $g=1.99$, $D=4.15$ cm^{-1} for the mononuclear complex, and $J=-3$ cm^{-1}, $g=2.05$, $D=-0.1$ cm^{-1} for the dinuclear complex, indicating an effective antiferromagnetic interaction between the two metal ions. The Mössbauer studies yield: $D=0.45$ cm^{-1} for the mononuclear complex, and $J=-1.5$ cm^{-1}, $D=-0.20$ cm^{-1} for the dinuclear complex.

Introduction

Heteropolymetallic molecules sustain an intense interest since they present new properties arising from interactions between different metal centers, compared with homopolymetallic molecules. It is of fundamental importance to relate their magnetochemical and electronic properties with structural features. These systems can also be considered as models for biological active sites. For example, Cu(II)–Fe(III) containing dinuclear complexes [1] provide potential analogue compounds for a redox center of the cytochrome *c* -oxidase molecule, in which a copper(II) ion ($S=1/2$) is antiferromagnetically coupled to a heme iron(III) ($S=5/2$), in the resting state [2]. Until now, the proposed magnitude for the exchange interaction (*c.* 200 cm^{-1}) between the two metal centers has not been reproduced, and this offers a challenge for the bioinorganic chemist. No doubt, whatever the 'iron–(bridge)–copper' species are, more detailed understanding is required before the specific features of the 'cytochrome a$_3$–(bridge)–copper(II)' site can be readily established.

We have synthesized new copper(II)–iron(III) molecules which may be described as ferric acetylacetonate (acac) derivatives in which one or two acac in Fe(acac)$_3$ have been replaced by Cu(salen) or Cu(Mesalen) molecules acting as bidentate ligands [3, 4]. Such types of adduct structures have been described by Sinn and co-

---

*Abbreviations: salen: 1,2-bis(salicylideneamino)ethane; acac: acetylacetonate(1−).

**Also at the University of Lübeck.

†Authors to whom correspondence should be addressed.

0020-1693/92/$5.00

workers [5] who reported adducts of Cu(salen) with divalent metal complexes. Very few heteropolynuclear adducts have been described which contain the copper(II) ion and a trivalent ion [6]. Our interest in this type of complex has been stimulated by the formation of bonds between molecular entities being preexistent to the adduct formation. Taking advantage of this feature, we have performed an independent characterization of the mononuclear moieties. Then the adduct, when it is formed, should no longer present any monomeric properties, instead, it is expected that it exhibits new and specific properties, which may then be related to those of the monomers.

The adduct Cu(salen)Fe(acac)$_2$NO$_3$ is obtained when one acac from Fe(acac)$_3$ is replaced by Cu(salen). We present here its investigation by magnetic susceptibility, EPR and Mössbauer techniques. The corresponding precursor Fe(acac)$_2$NO$_3$ has also been obtained and characterized and its properties will be compared with the dinuclear derivative.

Replacing two acac by Cu(Mesalen) molecules, we have succeeded in synthesizing heterotrinuclear and heterotetranuclear clusters, the properties of which have been described separately [4].

Experimental

Synthesis

Fe(acac)$_2$NO$_3$

Fe(acac)$_2$NO$_3$ was prepared from reaction of stoichiometric amounts of tris(acetylacetonato)iron(III), Fe(acac)$_3$ and iron(III) nitrate, Fe(NO$_3$)$_3$. The precursor Fe(acac)$_3$ (1 mmol) was dissolved in a minimum volume of methanol. Iron nitrate (0.5 mmol) was then added to the solution, with stirring for 30 min. The product was obtained as a red–brown powder after the solution has been evaporated to dryness at room temperature, or after the solvent has been removed under vacuum. It is slightly sensitive to moisture but does not decompose; it was kept under nitrogen if not used immediately. Satisfactory elemental analyses were obtained for the freshly precipitated complex. *Anal.* Calc. for $C_{10}H_{14}NO_7Fe$: C, 37.99; H, 4.63; N, 4.43; Fe, 17.7. Found: C, 37.62; H, 4.63; N, 4.51; Fe, 17.4%. When the compound is exposed to moisture, analyses yield two additional water molecules, i.e. Fe(acac)$_2$NO$_3\cdot$2H$_2$O.

Cu(salen)Fe(acac)$_2$NO$_3$

This compound was prepared by reaction of the Schiff base Cu(salen) with the monomeric iron(III) species as described above. Cu(salen) was obtained according to literature procedures [7]. Cu(salen) (0.3 mmol) was dissolved in 250 ml of dichloromethane, at reflux temperature. Fe(acac)$_2$NO$_3$ (0.3 mmol) dissolved in a minimum volume of methanol, was then added. The resulting solution was stirred and kept refluxing for 4 h. While at reflux temperature, the solution was concentrated by evaporating under a stream of nitrogen until the product separated as a black microcrystalline powder. The solution was hot filtered and the precipitate dried under vacuum. *Anal.* Calc. for $C_{28}H_{28}N_3O_9CuFe$: C, 48.33; H, 4.34; N, 6.50; Cu, 9.84; Fe, 8.65. Found: C, 48.34; H, 4.51; N, 6.62; Cu, 9.34; Fe, 8.26%.

Magnetic measurements

Magnetic susceptibility data were collected on powdered samples weighing about 4 mg. The experiments utilized a variable temperature (4.2–300 K) Faraday type susceptometer equipped with an Oxford Instruments continuous flow cryostat. Diamagnetic corrections for the constituents were taken from literature data. The fittings to the experimental data were carried out by minimizing the R factor defined as $R = \Sigma[\chi_M^{obs} - \chi_M^{calc}]^2/\Sigma[\chi_M^{obs}]^2$.

EPR spectroscopy

Electron paramagnetic resonance spectra were recorded at X-band frequency using a Bruker ER-200D spectrometer, also equipped with an Oxford Instruments continuous flow cryostat (4.2–300 K). The magnetic field was determined with a Hall probe and the klystron frequency with a Hewlett-Packard frequency meter.

Mössbauer spectroscopy

The same equipment was used as described previously [4].

IR and powder X-ray diffraction

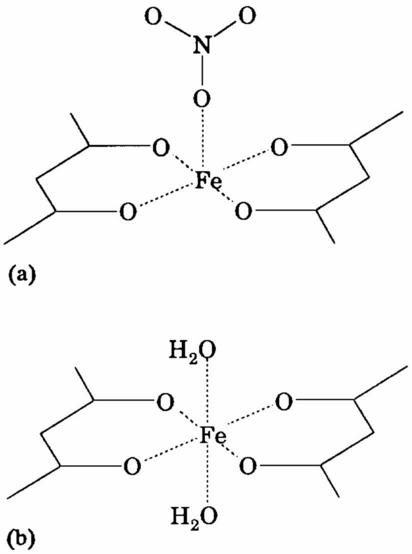
Standard IR methods were used in order to determine changes in bands of the reactant compounds. X-ray Debye–Scherrer diagrams of the resulting compounds were taken to make sure that characteristic patterns of the reactants were absent after adduct formation.

Results and discussion

Structural information

Fe(acac)$_2$NO$_3$

We propose the structure illustrated in Scheme 1(a) due to the arguments given below. IR bands were identified by comparing the spectrum with the one of Fe(acac)$_3$ for the acac bands and with the spectra of sodium and iron nitrates in order to elucidate the nitrate binding. In addition to the characteristic bands of the acac ligand, the spectrum displays four bands,



Scheme 1.

three of them intense at 1380, 1250, 1010 cm^{-1} and one of less intensity at 820 cm^{-1}. In the hydrated form, the two bands at 1250 and 1010 cm^{-1} vanish, the band at 1380 cm^{-1} remains unchanged and the one at 810 cm^{-1} becomes more intense, these two bands being also observed in the ionic nitrates [8]. Those bands are unambiguously due to the nitrate vibration. They indicate that in the non-hydrated complex, the nitrate is coordinated to the iron, whereas it is ionic in the hydrated one. Although IR could not be used to determine whether water is coordinated or not, the two water molecules, in the hydrated complex, probably achieve the hexacoordination around the iron ion, shown in Scheme 1(b).

In order to elucidate the problem whether nitrate is uni- or bidentate coordinated to iron, we recorded EPR spectra at 4.2 K of both the hydrated and the non-hydrated complexes in solid state, and in addition of a freshly prepared methanolic solution of $Fe(acac)_2NO_3$ (Fig. 1). For a unidentate ligand, one should expect the EPR spectra to reflect axial ligand-field symmetry at the iron site, while bidentate coordination of nitrate should produce considerable rhombic distortion of the ligand field. As a reference for a complex without bidentate ligands, we used the hydrated complex. The strong similarities of the EPR spectra of the complex in the non-hydrated and hydrated form (Fig. 1(a) and (b)) reflect almost identical spatial ligands arrangements, irrespective whether nitrate or water is coordinated to the metal ion. In both spectra the resonances around $g \approx 6$ and 2 are typical for ferric iron ($S = 5/2$) in axially symmetric ligand field. This observation suggests that the nitrate probably is a unidentate axially bound ligand in $Fe(acac)_2NO_3$, with the two acac close to the *trans* configuration. Such an oxygen pentacoordination is unstable and exposure to moisture leads to the more stable hexacoordination.

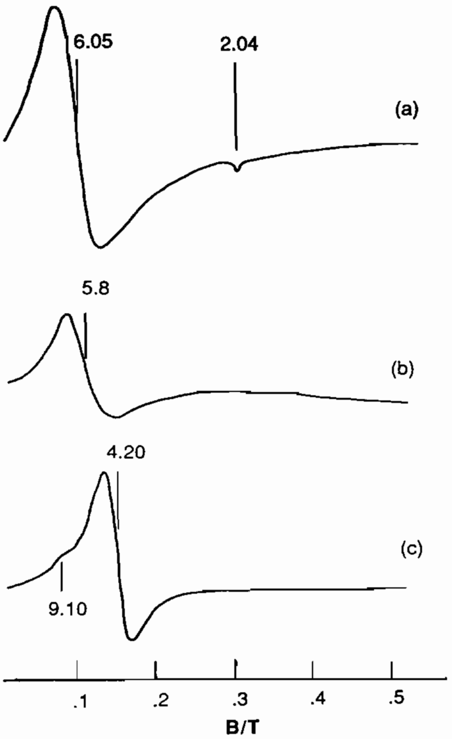
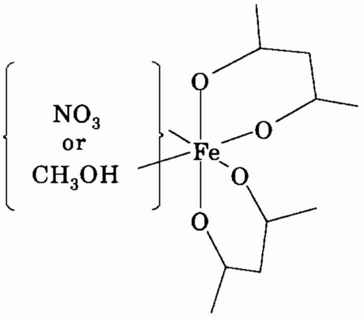


Fig. 1. X-band EPR spectra for the complex $Fe(acac)_2NO_3$ at 4.2 K: (a) solid state spectrum of the non-hydrated form; (b) solid state spectrum of the hydrated form; (c) spectrum in methanolic solution. Effective *g* values are indicated.



Scheme 2.

In the methanol solution (Fig. 1(c)) a single and broad signal is observed at $g \approx 4.3$ which is a characteristic feature of the isotropic resonance arising from the middle Kramers doublet of an $S = 5/2$ ion subject to zero-field splitting of maximum rhombic distortion [9]. The two acac probably move to positions close to *cis* configuration, whereas the nitrate remains monodentate to the iron, and a methanol molecuule is now bound or the nitrate is bidentate, favoring a possible further substitution by other bidentate ligands (Scheme 2).

The observations provided by both IR and EPR experiments suggest a possible rearrangement of the ligands when going from solution to solid state; they also indicate the pathway of formation of the binuclear adduct, the proposed structure of which can be derived from that of the mononuclear iron complex in solution.

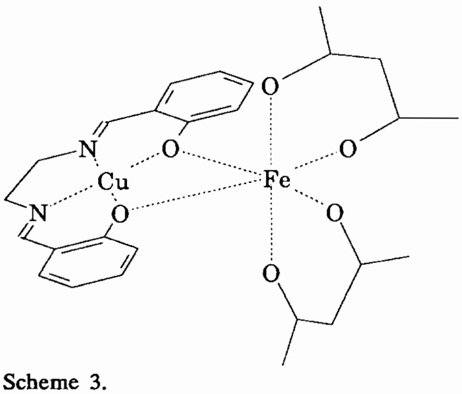
Cu(salen)Fe(acac)$_2$NO$_3$

The IR spectrum of the molecule is considerably modified with respect to the ones of the two mononuclear species. The most striking feature is the disappearance of the band at 1540 cm^{-1}. This band is characteristic of the phenolic oxygen stretching in the copper containing molecule, which has been shown to be shifted to higher energies when the phenolic oxygen atoms bridge two metal ions. The band at 1380 cm^{-1} characterizing the ionic nitrate, as well as the acac bands, remain unchanged. From this IR spectrum it can be concluded that the nitrate ion is no longer bound to the iron and that the coordination of the acac group is unchanged. The phenolic stretching is probably modified so that it cannot be identified; therefore from IR data, the oxygen atoms as donors to the iron ion cannot be confirmed. Nevertheless, according to the proposed structure for the mononuclear complex in solution (Scheme 2) a possible structure of the dinuclear unit is shown in Scheme 3 suggesting that the hexacoordination around the iron is achieved by two acac groups and one Cu(salen) molecule acting as a bidentate ligand. The reported structures of the heterotetranuclear complex as well as of the trinuclear molecule in ref. 4 reinforce the structural proposition given here for the dinuclear unit.

Magnetic properties

Fe(acac)$_2$NO$_3$

Magnetic susceptibility measurements have been performed on the non-hydrated complex in the solid state. The temperature dependence of the effective magnetic moment μ_{eff} (in units of the Bohr magneton: μ_B) is shown in Fig. 2. A Curie-law behavior which corresponds to a constant μ_{eff} value of 5.89 μ_B ranges from room temperature down to around 20 K. Then a decrease caused by the fine structure of the iron(III) ground state is observed down to 4.2 K, where the magnetic moment takes the value of 5.5 μ_B.



Scheme 3.

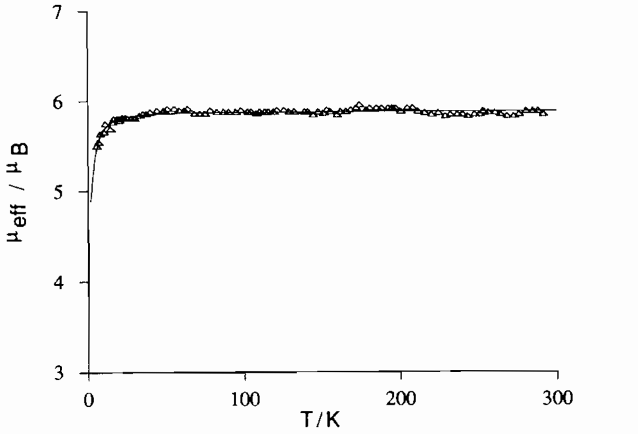


Fig. 2. Effective magnetic moment data for the mononuclear complex Fe(acac)$_2$NO$_3$ over the temperature range 4.2–300 K. The solid line is a spin-Hamiltonian simulation (see Text).

The usual spin-Hamiltonian formalism [10] associated with a high spin $S=5/2$ ground state has been considered: $\mathscr{H}=S(D)S+\beta S(g)B$. An axial zero-field splitting parameter D and an isotropic g factor have been introduced for simulating the magnetic susceptibility. A least-squares fit to the data leads to the following values of these two parameters: $g=1.99$, $D=4.15$ cm^{-1}.

Since the crystal structure is not available, we have not considered any intermolecular interaction. It is probable that taking into account such interaction would slightly reduce the obtained D value. Indeed, the Mössbauer study reported below, which has been performed in solution, leads to a smaller value (see Table 1).

Cu(salen)Fe(acac)$_2$NO$_3$

The temperature dependence of the molecular effective magnetic moment of this complex is displayed in Fig. 3. A Curie-law behavior describes the magnetic properties in the temperature range 300–80 K, the constant magnetic moment being equal to 6.26 μ_B. Then a decrease is observed with decreasing temperature from 80 to 4.2 K leading to a low-temperature magnetic moment of 5.2 μ_B at 4.2 K.

In the high-temperature range, where the Curie law is observed, the experimental μ_{eff} value is near the value corresponding to the presence of two independent iron(III) and copper(II) ions. In this case, μ_{eff} would be equal to the calculated value of 6.16 μ_B obtained from the local experimental g values ($g_{\text{Fe}}=1.99$ from the magnetic properties of the iron moiety and $g_{\text{Cu}}=2.12$ from the EPR spectrum of the copper(salen) molecule). But, by looking at the low-temperature range and

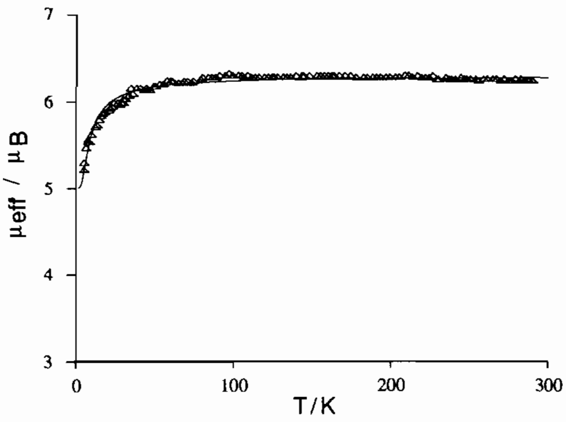
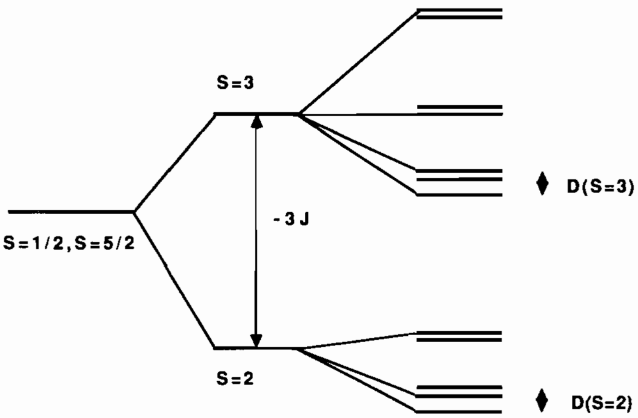


Fig. 3. Effective magnetic moment data for the dinuclear complex Cu(salen)Fe(acac)$_2$NO$_3$ over the temperature range 4.2–300 K. The solid line is the fit to the magnetic data of the susceptibility equation, derived from the model described in the text, and according to least-squares minimization procedures.



Scheme 4.

comparing with the data of the mononuclear complex, it is obvious that the properties of the dinuclear unit cannot be explained as the sum of those of the two individual moieties. An antiferromagnetic interaction is then supposed to be effective, which in addition, would confirm the presence of a dinuclear unit.

The data have been analyzed by using Griffith's model [11]. Two energy levels with $S=2$ and $S=3$ arise from the antiferromagnetically coupled $S_{Cu}=1/2$–$S_{Fe}=5/2$ pair, as described in Scheme 4. Their energy gap is equal to $3J$, derived from the exchange Hamiltonian $\mathcal{H}=-JS_{Cu}S_{Fe}$, supposing that zero-field splitting is much weaker than exchange interaction. Following Griffith's proposition, we have considered that zero-field splitting of the two multiplets of total spin $S=2$ and $S=3$ is essentially due to the local properties of the iron ion and neglected anisotropic coupling terms which were taken into account for the interpretation of the EPR $g=12$ signal measured in oxidized cytochrome *c* oxidase [12]. We have also neglected any rhombicity effect. Finally, the *g* factors associated with the two energy levels have been considered as identical because their values, which can be obtained from local *g* values (in the approximation of well separated spin manifolds [13],

$$g_{S=2}=(7g_{Fe}-g_{Cu})/6, \quad g_{S=3}=(g_{Cu}+5g_{Fe})/6$$

are indeed very close. Since the mean value for g_{Cu} obtained for the Cu(salen) molecule is equal to 2.12 and the corresponding value for g_{Fe} has been found equal to 1.99, the above relations lead to the values $g_{S=2}=1.97$ and $g_{S=3}=2.01$. Such a small difference can hardly be determined from magnetic susceptibility measurements.

Consequently, the following spin Hamiltonian has been considered:

$$\mathcal{H}=-JS_{Cu}S_{Fe}+D(S_{zFe}^2-1/3S_{Fe}^2)+g\beta SB \quad (1)$$

each term having the usual meaning.

The derived susceptibility equation has then been fitted to the data. The best fit obtained with an *R* factor equal to 5×10^{-5} leads to the following values of the spin-Hamiltonian parameters: $J=-3.0$ cm^{-1}, $D=-0.1$ cm^{-1} and $g=2.05$.

A weak antiferromagnetic interaction is thus observed in the dinuclear molecule, much weaker than the one proposed in cytochrome *c* oxidase [2]. Despite lacking knowledge of the crystal structure, the supposed nearly octahedral environment of the iron ion will probably favor ferromagnetic interactions of the active electron pairs against antiferromagnetic interactions [14]. The local *D* value is of the same order of magnitude, though of opposite sign, compared to the one found for the mononuclear entity in solution, again in agreement with the proposed structures for both molecules, and it is much smaller than the *D* value found in the solid state. We have to underline here again that we have not taken into account any intermolecular interactions which would slightly modify our results. At this point we want to emphasize that a negative *D* value has been found from a fit of the EPR data for the *g*12 signal in oxidized cytochrome *c* oxidase [12]. The obtained *g* factor shows a difference with the expected one: such a difference lies in the range of systematic errors of the technique used.

All the parameters presented here are of the same order of magnitude as those deduced from the Mössbauer study reported below, which contributes in supporting the chosen models.

Mössbauer spectroscopy

Fe(acac)$_2$NO$_3$ in frozen methanol solution

The Mössbauer spectra of the compound recorded at 1.5, 4.2 and 20 K under 2.47 T applied parallel to

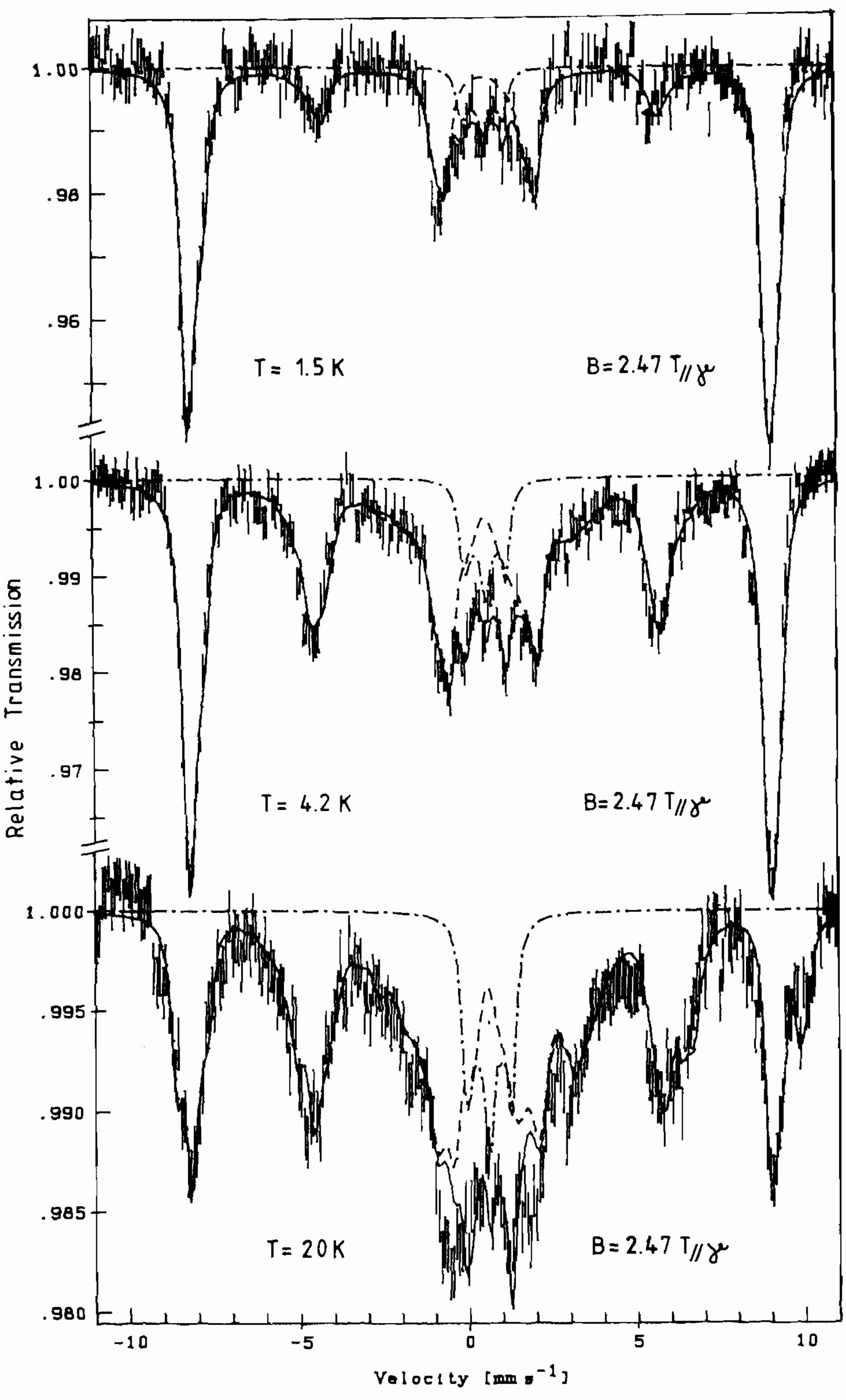


Fig. 4. Mössbauer spectra of Fe(acac)$_2$NO$_3$ recorded under 2.47 T applied parallel to the γ-rays at 1.5, 4.2 and 20 K. The dash-dotted lines correspond to a minor contribution of diamagnetic iron.

the γ-rays and at 4.2 K under 1.22 T applied perpendicular to the γ-rays are shown in Figs. 4 and 5, respectively. They exhibit a magnetic hyperfine structure which consists of well resolved lines. A minor contribution arises from a compound which contains diamagnetic iron, identified by a corresponding simulation

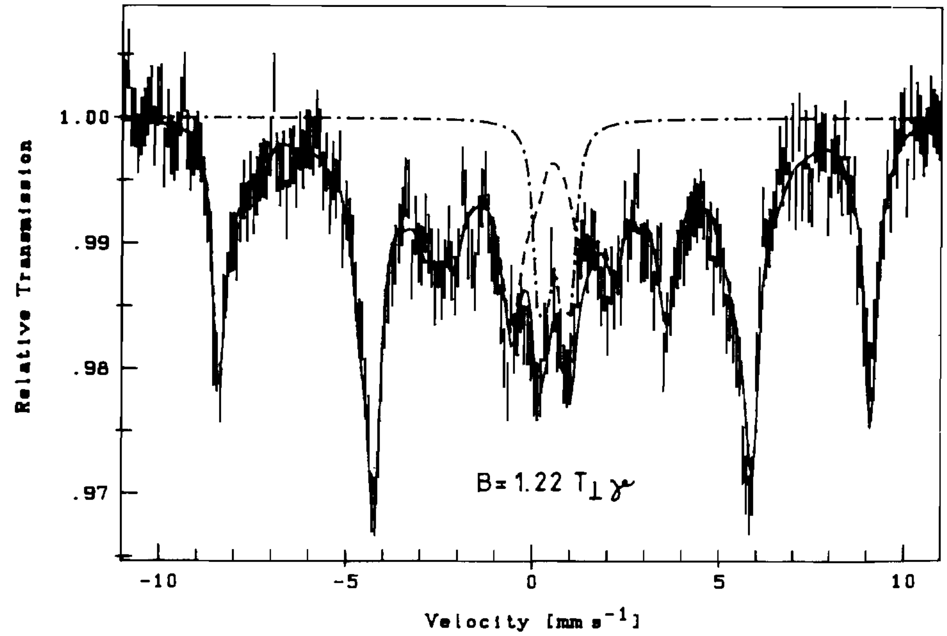


Fig. 5. Mössbauer spectrum of $Fe(acac)_2NO_3$ recorded under 1.22 T applied perpendicular to the γ-rays at 4.2 K. The dash-dotted lines correspond to a minor contribution of diamagnetic iron.

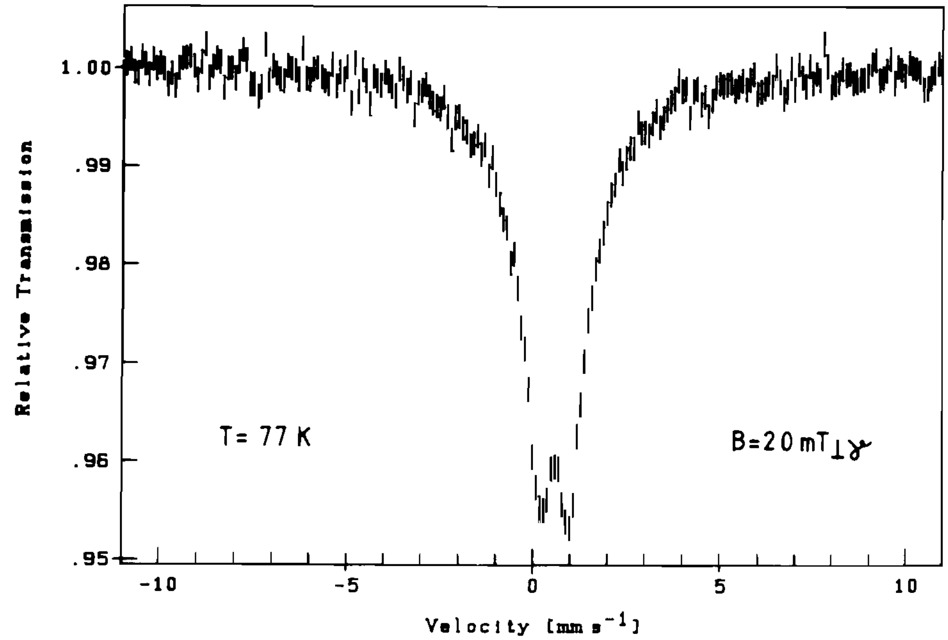


Fig. 6. Mössbauer spectrum of $Cu(salen)Fe(acac)_2NO_3$ recorded at 77 K under 20 mT applied perpendicular to the γ-rays.

(dash-dotted lines in Figs. 4 and 5). The data recorded under 2.47 T at different temperatures (Fig. 4) show that the overall magnetic splitting of about 17 mm s^{-1} is temperature independent. With an increase in temperature, the only observable effect is a stepwise equilization of the line intensities. Therefore the spectra can be considered as a superposition of subspectra from the three Kramers doublets of the spin state $S=5/2$ with their respective contributions being determined by corresponding Boltzmann factors. A similar behaviour has been observed previously by Debrunner and Schulz [15]. It suggests that the spin relaxation at low temperature is slow compared to the Larmor frequencies. Especially spin–spin relaxation is excluded, obviously, because the ions are paramagnetically diluted in the methanol solution.

Our attempt to analyze the spectra presented in Figs. 4 and 5 in terms of the spin-Hamiltonian formalism

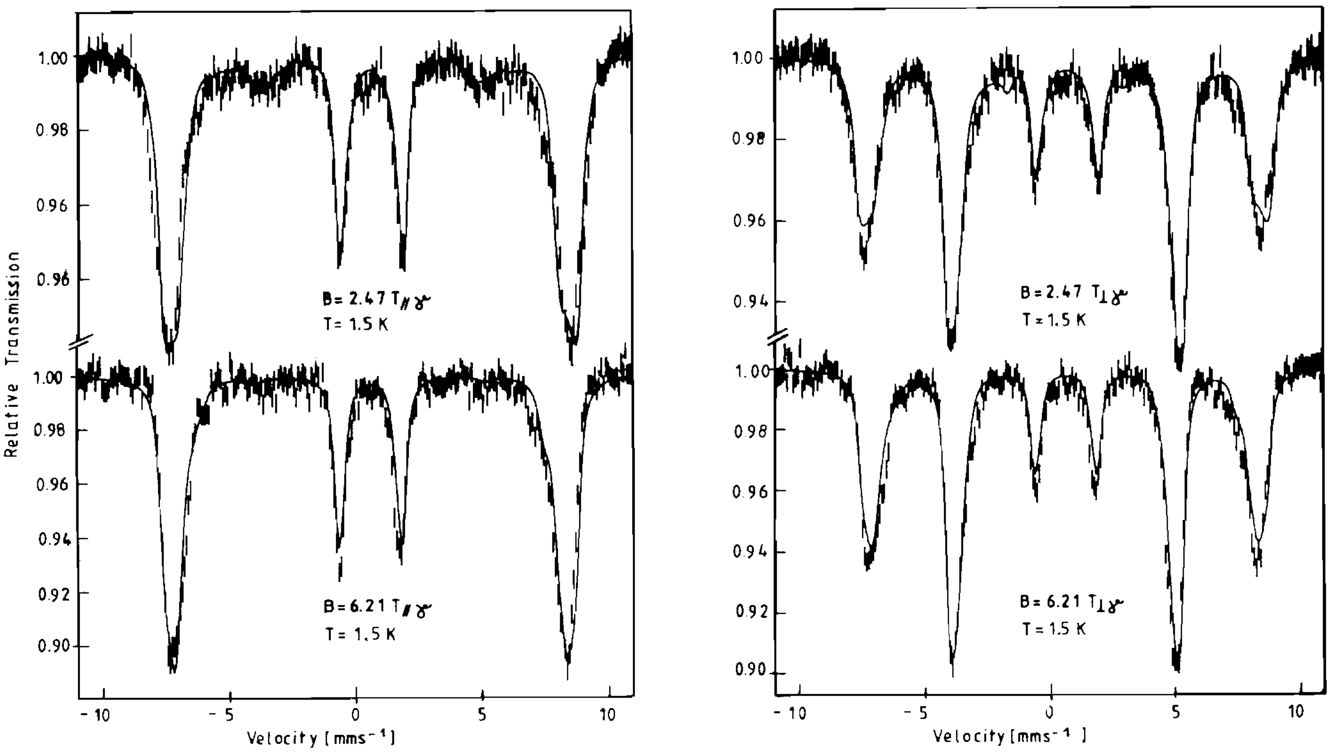


Fig. 7. Mössbauer spectra of Cu(salen)Fe(acac)$_2$NO$_3$ recorded at 1.5 K under 6.21 and 2.47 T applied parallel and perpendicular to the γ-rays.

for a single spin in the slow relaxation limit were successful:

$$\mathscr{H} = S(D)S + \beta S(g)B + S(A)I + H_Q - g_N\beta_N BI \qquad (2)$$

By reproducing the temperature dependence of the line intensities in the spectra recorded under 2.47 T, we could fix the sign of the main component of the electric field gradient (e.f.g.) tensor and zero-field splitting parameter D and, in addition, we were able to estimate the upper and lower limit for D. When the applied field is turned down to 1.22 T the crystal-field terms described by the parameters D and E/D gain more influence; hence, the final result $D = 0.45$ cm^{-1} has been obtained from the simulation under this condition which provided also a value for the rhombicity parameter $E/D = 0.31$ in agreement with the EPR results. The asymmetry parameter η and the Euler angles α and β of the e.f.g. tensor were obtained from the positions of the inner lines (from -5 to $+6$ mm s^{-1}). The outer lines, on the contrary, reflect the overall magnetic splitting (about 17 mm s^{-1}) which is sensitive to the y component of the magnetic hyperfine tensor, i.e. A_y, while A_x can be mainly deduced from the line shapes of the spectra recorded under 2.47 T (Fig. 4) and A_z from the inner region (-3 to $+4$ mm s^{-1}) of the spectrum recorded at 4.2 K under 1.22 T (Fig. 5). This corresponds to the procedure described by Debrunner and Schulz [15] for oxidized rubredoxin. The resulting spin-Hamiltonian parameters are summarized in Table 1.

Cu(salen)Fe(acac)$_2$NO$_3$

Under a weak applied field of 20 mT perpendicular to the γ-rays, which is a standard condition for mea-

TABLE 1. Parameters derived for Fe(acac)$_2$NO$_3$ and Cu(salen)Fe(acac)$_2$NO$_3$

	Fe(acac)$_2$NO$_3$	Cu(salen)Fe(acac)$_2$NO$_3$
δ^a (mm s^{-1})	0.60(3)	0.60(3)
ΔE_Q (mm s^{-1})	−0.70(5)	0.50(3)
Γ (mm s^{-1})	0.35(3)	0.35(3)
η	0.9(1)	0.9(1)
D(cm^{-1})	0.45(3)	−0.20(5)
E/D	0.31(3)	0.25(3)
g_x	2.00	2.00
g_y	2.00	2.00
g_z	2.00	2.00
A_{xx}(5/2)	−23.0(5)T	−21.2(5)T
A_{yy}(5/2)	−22.4(3)T	−21.2(3)T
A_{zz}(5/2)	−22.0(5)T	−23.0(5)T
J(cm^{-1})		−1.5
Euler angles (°) taking D tensor into e.f.g. tensor:		
α e.f.g.	90.0(5)	90.0(5)
β e.f.g.	90.0(5)	90.0(5)
γ e.f.g.	0.0	0.0

[a] Relative to α-Fe at r.t.

surements on ferric systems in order to have a definite axis of quantization [16], the spectrum of the complex shows a broad pattern at 77 K (Fig. 6). This most probably has to be attributed to spin–spin relaxation processes. We recorded a series of Mössbauer spectra at low temperature (about 1.5 K) under strong fields of 2.47 and 6.21 T applied parallel and perpendicular to the γ-rays (Fig. 7). This then enabled us again to analyze the experimental data with the spin-Hamiltonian formalism in slow relaxation limit.

We did not succeed in simulating the measured spectra in terms of the spin-Hamiltonian for a single spin alone, according to eqn. (2). In accordance with the results of the magnetic susceptibility study, the complex is characterized by a weak spin coupling between the two metal centers. Therefore we extended the spin-Hamiltonian by a term which comprises the coupling of the two spins $S_{Fe}=5/2$ and $S_{Cu}=1/2$, as shown in eqn. (1). Results of simulations with the parameters summarized in Table 1 are represented by solid lines in Fig. 7. They provide evidence for a weak antiferromagnetic coupling between the two metal spins which expresses itself quantitatively by a coupling constant $J=-1.5$ cm^{-1}.

It is now possible to confront parameters which we have obtained for the dinuclear complex with those valid for the monomer by looking at Table 1. Both sets are similar and typical for the high-spin ferric state.

Finally we wish to emphasize the complementarity of the three magnetic techniques we used.

Acknowledgement

This research was supported in part by NATO research grant no. 330/87.

References

1 (a) M. J. Gunter, L. N. Mander, K. S. Murray and P. E. Clark, *J. Am. Chem. Soc., 103* (1981) 6784–6787, and refs. therein; (b) J. T. Landrum, K. Hatano, W. R. Scheidt and C. A. Reed, *J. Am. Chem. Soc., 102* (1980) 6729; (c) S. E. Dessens, C. L. Merrill, R. J. Saxton, R. L. Ilaria, J. W. Lindsey and L. J. Wilson, *J. Am. Chem. Soc., 104* (1982) 4357–4361.

2 (a) M. Wikström, K. Krab and M. Saraste, *Cytochrome Oxidase: A Synthesis;* Academic Press, New York, 1981; (b) M. F. Tweedle, L. J. Wilson, L. Garcia-Iniguez, G. T. Babcock and G. Palmer, *J. Biol. Chem., 253* (1978) 8065; (c) T. H. Moss, E. Shapiro, T. E. King, H. Beinert and C. Hartzell, *J. Biol. Chem., 258* (1978) 8543.

3 I. Morgenstern-Badarau and H. H. Wickman, *Inorg. Chem., 24* (1985) 1889–1892.

4 I. Morgenstern-Badarau, D. Laroque, E. Bill, H. Winkler, A. X. Trautwein, F. Robert and Y. Jeannin, *Inorg. Chem., 30* (1991) 3180–3188.

5 (a) E. Sinn, *Coord. Chem. Rev., 5* (1970) 313–347; (b) C. J. O'Connor, D. P. Freyberg and E. Sinn, *Inorg. Chem., 18* (1979) 1077–1078, and refs. therein.

6 (a) A. Seminara, S. Guiffrida, A. Musumeci and I. Fragala, *Inorg. Chim. Acta, 95* (1984) 201–205; (b) D. W. Harrison, J. C. G. Bünzli, *Inorg. Chim. Acta, 109* (1985) 185–192.

7 P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Justus Liebigs Ann. Chem., 503* (1933) 84.

8 (a) K. Nakamoto, *Infra-red Spectra of Inorganic and Coordination Compounds,* Wiley–Interscience, New York, 1970; (b) B. Hathaway, *Comprehensive Coordination Chemistry,* Pergamon, Oxford, 1987, Ch. 2, p. 413.

9 (a) H. H. Wickman, M. P. Klein and D. A. Shirley, *J. Chem. Phys., 42* (1965) 2113–2117, and refs. therein; (b) W. Hagen, *Biochim. Biophys. Acta, 708* (1982) 82–98.

10 A. Abragam and B. Bleany, *Electron Paramagnetic Resonance of Transition Ions,* Oxford University Press(Clarendon), Oxford, 1970.

11 J. S. Griffith, *Mol. Phys., 21* (1971) 141–143.

12 G. W. Brudwig, R. H. Morse and S. I. Chan, *J. Magn. Reson., 67* (1986) 189–201.

13 (a) E. J. Buluggiu, *Phys. Chem. Solids, 41* (1980) 1175–1180; (b) R. P. Scaringe, D. J. Hodgson and W. E. Hatfield, *Mol. Phys., 35* (1978) 701–713; (c) W. B. Euler, *Inorg. Chem., 25* (1986) 1871–1875.

14 (a) P. W. Anderson, *Phys. Rev., 79* (1950) 350; (b) J. B. Goodenough, *Phys. Rev., 100* (1955) 564.

15 P. Debrunner and C. Schulz, in I. J. Gruverman and C. W. Seidel (eds.), *Mössbauer Effect Methodology,* Plenum, New York, 1976.

16 A. M. Afanas'ev and Y. M. Kagan, *JETP Lett., 8* (1968) 382.