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Mesomorphic properties and magnetic behaviour of di-(5-substituted-salicylidene)ethylenediaminato cobalt(II) complexes

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The result of optical X-ray, DSC and magnetic susceptibility studies of new Co(II) metallomesogens are reported. The di-(5-substituted-salicylidene)ethylenediaminato cobalt(II) complexes exhibit broad range S_A phases. A comparison with corresponding copper(II) and nickel(II) complexes leads to conclusions about how the properties are influenced by the metal atom. Cobalt(II) complexes of this kind form different modifications which are either active or inactive against oxygen. The conversion process (inactive–active) is monitored by time dependent X-ray diffractometric measurements.

1. Introduction

Research in the field of metallomesogens is rapidly developing. An increasing number of ligands has been found to be suitable for forming liquid crystals by incorporating metal atoms [1]. In some cases, these kinds of liquid crystal often have a rather low thermal stability. Therefore many of those compounds are not useful for a clear characterization of the properties of the liquid crystalline state. Because of this, it is necessary to know much more about structure–property relationships for metallomesogens in order to obtain lower melting, stable substances with broad mesophase ranges.

The influence of the metal atom on the properties of the liquid crystalline materials is very important, not only with respect to the colour of the complex formed, but also with regard to the possible magnetic molecular interactions. Finally, it should also be reflected in the phase behaviour and the stability of the complexes.

A ligand very useful in the study of these correlations is provided by Schiffs bases derived from salicylaldehyde. The complexes of Schiffs base derivatives of 4-substituted salicylaldehydes have been studied in detail, and many correlations between structure and liquid crystalline properties have been established [1–4].

In continuation of our work on di-(5-substituted-salicylidene)ethylenediaminato complexes, we have prepared the corresponding cobalt(II) chelates, and are now able to make interesting comparisons between the Co(II), Ni(II) and Cu(II) complexes, drawing conclusions as to how the properties are influenced by the metal atom.

2. Experimental

The synthetic route is similar to that used for the preparation of the analogous Ni(II) and Cu(II) chelates [5, 6], but the conversion of the ligands to the complexes turned out to be more complicated. As discussed below in more detail, complexes of this kind form different modifications. Only one of them is inactive against oxygen. For the investigation of the mesomorphic properties of the desired Co(II) complexes, we had to make sure that the pure inactive modification was obtained exclusively. We regarded this a prerequisite for the reproducibility of our investigations.

The cobalt(II) acetate tetrahydrate was boiled with ethyl alcohol until all the crystalline solid had been converted into a pink amorphous powder (N_2 was bubbled through the solution). This mixture was added to the solution of the Schiffs base **I** (N_2-atmosphere). On cooling the solution, small reddish brown crystals precipitated. In this manner,

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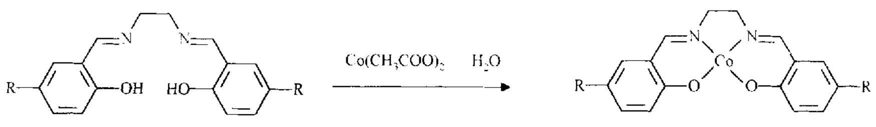
Figure 1. Reaction scheme.



I

II: $R = C_nH_{2n+1}$
III: $R = C_nH_{2n+1}O$

Table 1. Elemental analyses of di-(5-alkylsalicylidene)ethylenediaminato cobalt(II) complexes.

Compound	n	Molecular formula	Elemental analysis (Calc.) per cent C	H	N
IIa	5	$C_{26}H_{34}N_2O_2Co$	67·24 (67·07)	7·13 (7·37)	5·91 (6·02)
IIb	6	$C_{28}H_{38}N_2O_2Co$	67·93 (68·12)	7·91 (7·76)	5·74 (5·68)
IIc	8	$C_{32}H_{46}N_2O_2Co$	69·57 (69·91)	8·21 (8·44)	5·18 (5·10)
IId	9	$C_{34}H_{50}N_2O_2Co$	70·61 (70·67)	8·67 (8·73)	4·94 (4·85)
IIe	10	$C_{36}H_{54}N_2O_2Co$	71·19 (71·36)	9·12 (8·99)	4·80 (4·63)

Table 2. Elemental analyses of di-(5-alkyloxysalicylidene)ethylenediaminato cobalt(II) complexes.

Compound	n	Molecular formula	Elemental analysis (Calc.) per cent C	H	N
IIIa	5	$C_{26}H_{34}N_2O_4Co$	62·59 (62·75)	6·80 (6·89)	5·61 (5·63)
IIIb	6	$C_{28}H_{38}N_2O_4Co$	64·09 (63·97)	7·38 (7·29)	5·21 (5·33)
IIIc	7	$C_{30}H_{42}N_2O_4Co$	64·88 (65·07)	7·52 (7·65)	5·17 (5·06)
IIId	8	$C_{32}H_{46}N_2O_4Co$	65·91 (66·06)	8·08 (7·98)	5·01 (4·82)

which is very similar to the method of West [7], we prepared the cobalt(II) complexes **II** and **III**.

In connection with the investigations of the magnetic behaviour, we also prepared the active modification of certain complexes (**IIIc, IIId**) according to the method described by Pfeiffer *et al.* [8]. In order to make these compounds distinguishable from the inactive modifications, we have added an (**a**) after the number of the compounds in the discussions below.

The complexes were analysed without recrystallization, since oxygen was absorbed rapidly by solutions in all solvents. The elemental analyses data are presented in tables 1 and 2. The compounds **II** and **III** were examined by optical microscopy (Linkam THM 600/S Nikon Optiphot-2) and DSC (Perkin–Elmer DSC-7). The results are shown in tables 3 and 4.

The X-ray diffractometric measurements were performed using a focusing, horizontal, two circle X-ray diffractometer (STOE STADI 2) with a modified oven to assess the temperature dependent scattering data. The X-ray source was a long fine focus X-ray tube (Siemens FK), with a line focus of $0{\cdot}4 \times 12\,mm^2$. The CuK_{α_1} radiation ($\lambda = 1{\cdot}54056\,Å$) was focused by a curved Ge(111) monochromator. The mechanically and electrically controlled smallest step width of the diffractometer in the 2θ and ω circle was 0·001°. For fast diffractometry, a linear position-sensitive detector (STOE Mini PSD) was used with a resolution of the step; width of 0·01° in the 2θ circle.

The magnetic susceptibilities, as functions of temperature, of the powdered metallomesogens were recorded using a Faraday-type magnetometer [9]. For the measurements presented, an improved system compared to that in [9] was used (computer controlled Cahn D-200 microbalance, Bruker B-MN 200/60 power supply). the applied field was about 1·2 T. The magnetic susceptibilities of the compounds in the temperature range 300–500 K were obtained using the heating mode of the system especially designed for this range. Diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constant [10]. Magnetic moments were obtained using $\mu_{eff}/\mu_B = 2{\cdot}828(\chi T)^{1/2}$.

3. Results and discussion

The substances form deep red crystals. The high temperature phase was identified as a S_A phase by texture

Table 3. Transition temperatures (K) and enthalpies (kJ mol) for the cobalt complexes (II).

Compound	n	C_1		C_2		C_3		S_A		I
IIa	5	●		—	401 (10·5)	●	514 (9·4)	●	581	●
IIb	6	●		—	412 (11·6)	●	535 (10·2)	●	570	●
IIc	8	●		—	395	●	488	●	556	●
IId	9	●	342 (45)	●	374 (15·6)	●	471 (10·4)	●	542 (6·9)	●
IIe	10	●		—	385 (22·1)	●	463 (11·1)	●	528 (7·2)	●

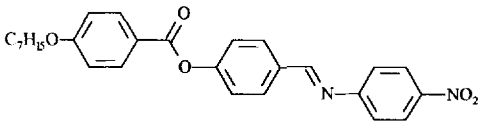
Table 4. Transition temperatures (K) and enthalpies (kJ mol^{-1}) for the cobalt complexes (III).

Compound	n	C_1		C_2		C_3		S_A		I
IIIa	5	●		—	394 (12·4)	●	509 (8·9)	●	583	●
IIIb	6	●		—	402	●	470	●	568	●
IIIc	7	●		—	413	●	458	●	565	●
IIIc(a)	7	●		—	408 (14·7)	●	458 (11·7)	●	564 (7·8)	●
IIId	8	●		●	410	●	446	●	551	●
IIId(a)	8	●	341 (3·9)	●	398 (12·7)	●	446 (9·4)	●	550	●

(a) = active modification.

observations. This has been proved by miscibility and X-ray studies. The DSC trace of compound **IIIc** (see figure 2) is shown as an example, and displays several transitions.

Compound **IIIa** was mixed with compound **IV** of conventional rod-like molecular form, which exhibits a S_A phase. Complete miscibility was observed between the high temperature phase and the S_A phase of the reference substance. The X-ray pattern of non-oriented samples of substance **IIId** exhibits the characteristic features of an S_A phase. The existence of several orders of the inner reflection proves the formation of a layer structure. The corresponding *d*-values agrees well with the length of the molecule in its fully extended form, estimated as 21 Å. Therefore the structure of the high temperature phase of this metallomesogen must be considered to be that of a conventional S_A phase.



IV C 400 S_A 501·5 N 528 I

At lower temperatures, a phase called C_3 exists; this could be classified on the basis of X-ray studies at a crystalline phase. Further investigations are however necessary to check the possibility of an S_E(dimer)$\rightarrow$$S_A$(monomer) transition, as in the case of similar nickel complexes[11]. Time dependent X-ray diffractometric measurements of the inactive form of compound **IIId** were carried out at 423 K. The time dependent diffraction profiles are represented in figure 3. At the beginning we observed a strong inner reflection at the angle $2\theta = 2{\cdot}516$ ($d = 35{\cdot}08$ Å), which decreases continuously in intensity over a few hours, while a new inner reflection appears at $2\theta = 3{\cdot}124$ ($d = 28{\cdot}25$ Å), as indicated in figure 3. It is quite evident that a phase transition between two different structural arrangements occurs, and this will be discussed later. Comparison between the di-(alkyloxysalicylidene)ethylenediaminato cobalt(II) complexes III and the corresponding nickel(II) and copper(II) complexes [5, 6] could possible provide an answer concerning the influence of the metal atom on the properties of the complexes (see figures 4, 5 and 6). The shapes of the molecules are almost the same, and it should be possible to trace property differences back to the electronic influences of the metal on the intermolecular interactions.

It becomes clear that the cobalt and nickel complexes exhibit almost the same behaviour. The broad S_A ranges and the decreasing clearing and melting temperatures with chain length indicate that they are very much akin to each other. In comparison to these compounds, the behaviour of the copper(II) complexes (see figure 6) is different. They do show the S_A phase, but the mesophase stability is lower and the melting temperatures are up to 70 degrees higher than in case of the nickel and cobalt compounds. Furthermore there is no significant change in the clearing and melting temperatures on lengthening the alkyloxy chains. From X-ray investigations of similar complexes [12–4], we know that copper(II) tends to form axial interactions with oxygen atoms of neighbouring molecules. The resulting molecular interactions generate the comparatively high melting temperatures and also give an explanation for other drastic decrease in the thermal stability after the transition to the S_A phase. In the S_A phase the molecules are forced to lie parallel in layers and the stabilization of the copper chelate by axial interactions involving a neighbouring oxygen is no longer possible. Finally we can conclude that the type of mesophase is determined by the shape of the molecule, whereas the

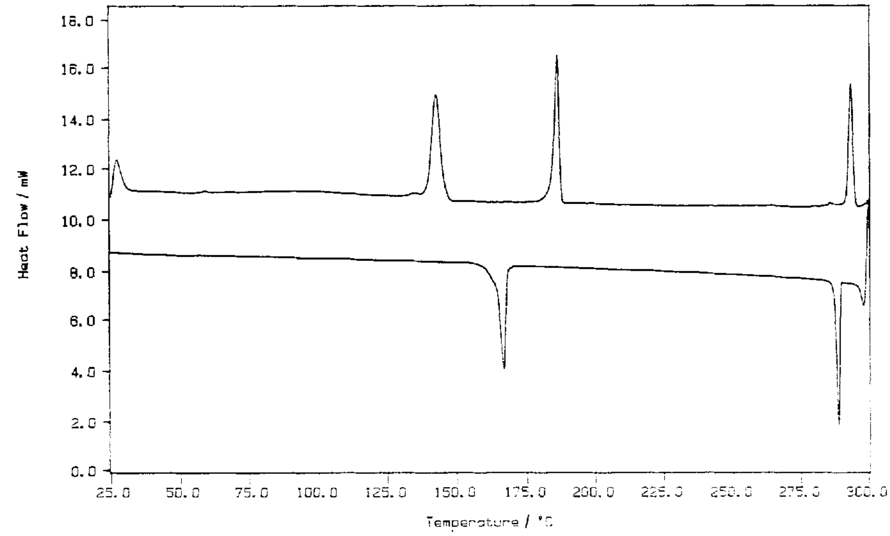


Figure 2. Differential scanning calorimetry thermogram for compound **IIIc**.

mesophase range and the melting and clearing temperatures are mainly affected by the metal atom.

4. Magnetic behaviour

The temperature dependent magnetic susceptibility and magnetic moment data in the temperature range 4·2–500 K for compound **IIIc(a)** (active form) are displayed together with the phase transition temperatures in figure 7 (*a*); figure 7 (*b*) presents the data starting from 300 K. The data for compound **IIId** and **IIId(a)** are given in figure 8 (inactive form) and figure 9 (active form). The μ_{eff} values at room temperature (2·3–2·5 μ_{B}) for complexes **IIIc(a)**, **IIId** and **IIId(a)** clearly exclude tetrahedral or octahedral coordination around the cobalt (II), and suggests a square-planar of square-pyramidal coordination. The tetradentate ligand usually provides planar coordination, but a square-pyramidal coordination can be realized by axial interactions between nitrogen or oxygen atoms from adjacent molecules.

The structure of the related non-mesomorphic compound Co[Salen] consists of dimeric units [15, 16]. This dimerization is realized due to the presence of axial interactions between cobalt(II) atoms and phenolic oxygen atoms in adjacent pairs of molecules. The variation in oxygenation activity (which leads to the classification into active and inactive forms) has been related to the presence of voids in the crystal lattice, sufficient in size to allow the passage of oxygen [17]. The active form is presumed to contain $[\mathrm{Co(salen)}]_2$ dimeric units with an open lattice packing relative to the inactive form [15].

In our case, direct synthesis as described above, yields the inactive form, which can be converted into the active from by recrystallization. Heating the inactive form at 420 K for some hours also leads to a product which

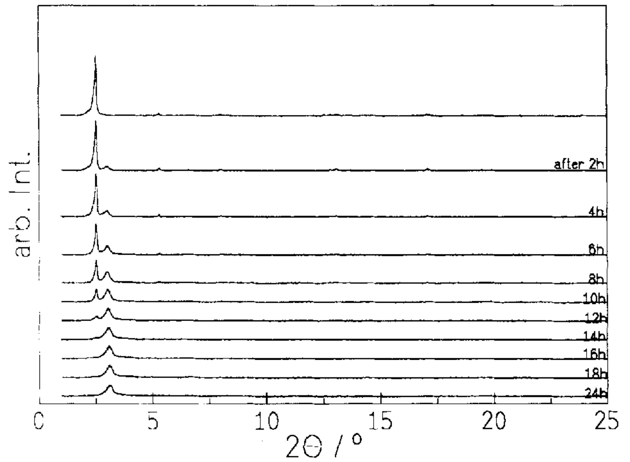


Figure 3. Time-dependent diffraction profiles for compound **IIId**.

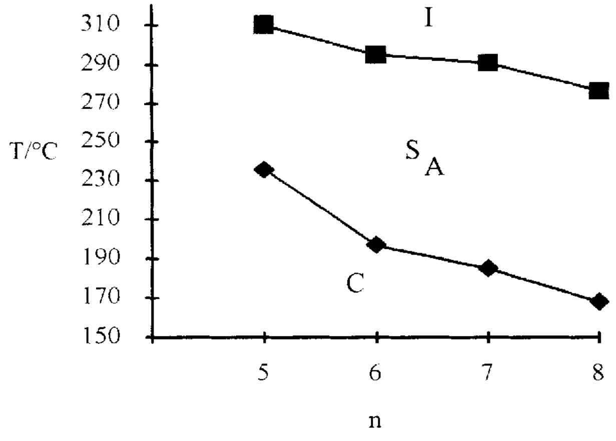


Figure 4. Transition temperatures of the di-(5-alkoxysalicylidene) ethylenediaminato Co(II)complexes as a function of alkyl chain length.

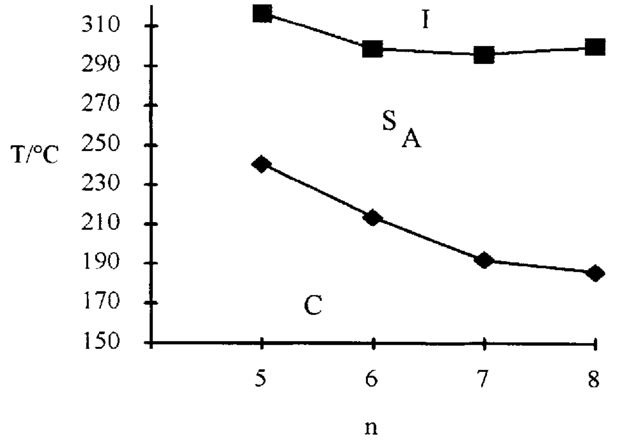


Figure 5. Transition temperatures of the di-(5-alkyloxysalicylidene) ethylenediaminato Ni(II)complexes as a function of alkyl chain length.

exhibits an identical DSC and magnetic behaviour to that of the directly obtained active form. This conversion process is shown by the time-dependent X-ray diffractometric experiments (see figure 3), and we can conclude that the initial state corresponds to the inactive form and the final state to the active form.

In order to prove if similar dimerization to that occurring in the case of Co[salen] is also present in compounds **IIIc(a)**, **IIId** and **IIId(a)**, we have fitted the $\chi(T)$ data for compound **IIIc(a)** to the well-known Bleaney–Bowers equation (1), assuming the dimeric nature of the complex,

$$\chi = (1 - x_{\mathrm{p}}) \frac{N_{\mathrm{L}} g^2 \mu_{\mathrm{B}}^2}{kT} \frac{\exp(2J/kT)}{1 + 3\exp(2J/kT)} + x_{\mathrm{p}} \frac{N_{\mathrm{L}} g^2 \mu_{\mathrm{B}}^2}{3kT} S(S+1) + N_{\alpha}, \qquad (1)$$

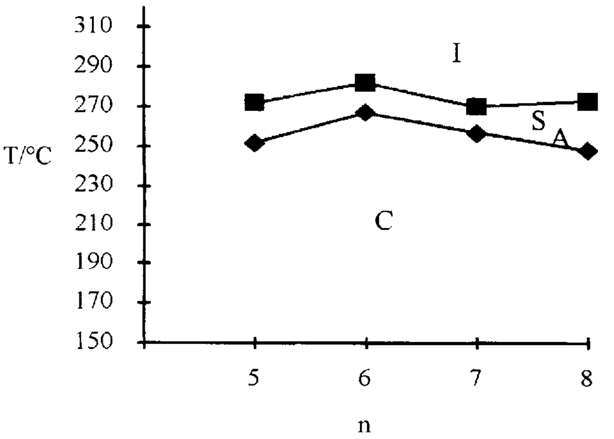
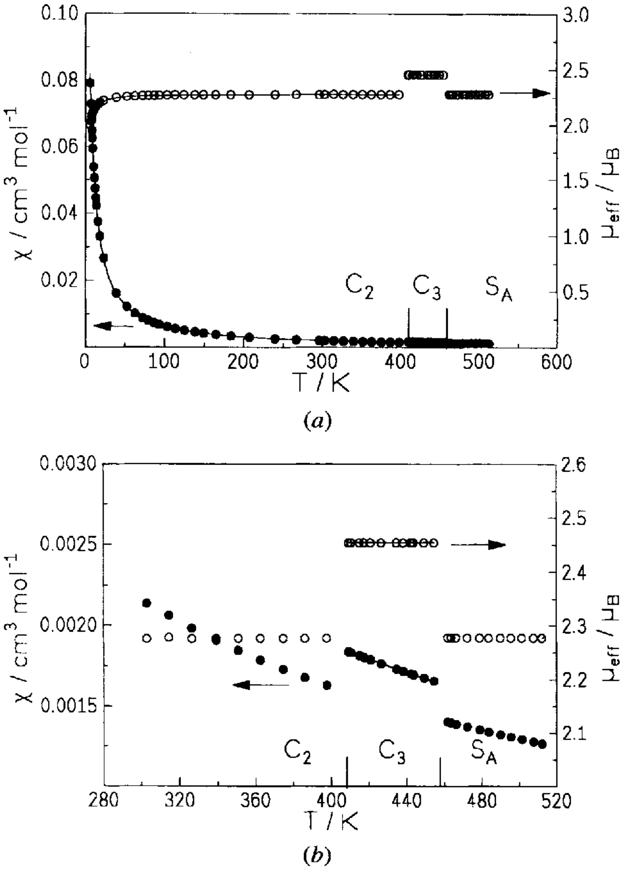


Figure 6. Transition temperatures of the di-(5-alkoxysalicylidene) ethylenediaminato Cu(II)complexes as a function of alkyl chain length.



(*a*)

(*b*)

Figure 7. (*a*) Experimental and calculated magnetic susceptibilities and magnetic moments of compound **IIIc(a)**. (*b*) Experimental and calculated magnetic susceptibilities and magnetic moments of compound **IIIc(a)** from 300 K.

where J corresponds to the spin-hamiltonian $\hat{\mathrm{H}} = -2J\hat{S}_1\hat{S}_2$. Here, the presence of monometic impurities (molar fraction x_{p}) and the temperature independent paramagnetism were also taken into account. Excluding the data for the C_3 phase, we obtain $g = 2{\cdot}63$, $J = -1{\cdot}8\,\mathrm{cm}^{-1}$, $x_{\mathrm{P}} = 2{\cdot}3$ and

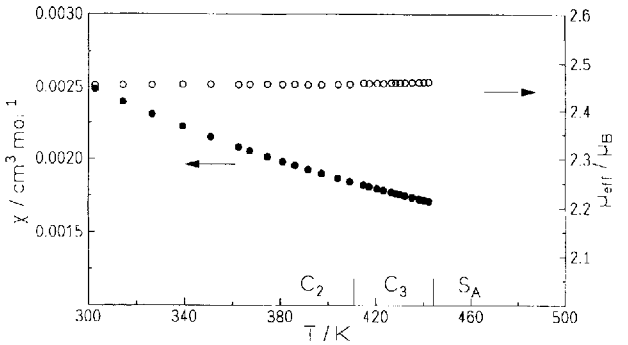


Figure 8. Experimental magnetic susceptibilities and magnetic moments of the inactive form of compound **IIId**.

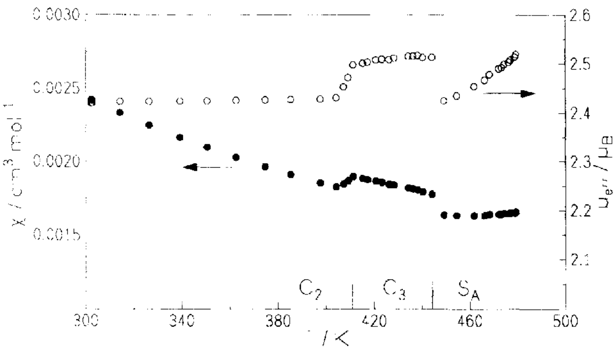


Figure 9. Experimental magnetic susceptibilities and magnetic moments of the active form of compound **IIId(a)**.

$N_\alpha = 367 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$. The slightly negative value of J reflects some degree of dimerization. However, the interactions are obviously not sufficient to provide such markedly high clearing and melting temperatures as in the related copper complexes. The susceptibility data displayed in figures 7 (*a*), (*b*) 8 and 9 for all compounds were corrected for the underlying temperature-independent paramagnetism ($N_\alpha = 367 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ per cobalt). The fitted values obtained describe the magnetic behaviour of the crystalline phases as well as the S_A phase of compound **IIIc(a)**. Compound **IIId(a)** exhibits a similar behaviour; the increase in μ_{eff} in the temperature range $T > 460\,\mathrm{K}$ is due to decomposition of the sample.

A significant feature of the magnetic behaviour is the shift of about $+0{\cdot}1\,\mu_B$, compared to the C_2 phase and the S_A phase, observed for the C_3 phase of the active forms of **IIIc(a)** and **IIId(a)**, whereas in the inactive form of **IIId**, no shift was observed. In contrast top the pronounced step in the case of compound **IIIc(a)**, we observed for compound **IIId(a)** a continuous increase in μ_{eff} with temperature at the phase transition C_2/C_3. Most probably, under our experimental conditions, the conversion process C_2/C_3 is not completely finished at the phase transition; consequently, a part of the sample remains which is still in the C_2 state. In the C_2 phase, the magnetic behaviour of the active and inactive forms **IIId(a)** and **IIId** is in principle identical. The increase in the magnetic susceptibility observed for the C_3 phase of the active forms **IIIc(a)** and **IIId(a)** may possibly be explained in terms of some structural changes, which, in detail, are unknown.

The small increase in μ_{eff} as a function of temperature is not essentially affected by the phase transition C_2–C_3. Accordingly, we have fitted the magnetic susceptibility data for compound **IIIc(a)** in the C_3 phase to the Bleaney–Bowers equation (1). The best fit parameters using equation (1) are $g = 2{\cdot}83(2)$, $J = -1{\cdot}9(1)\,\mathrm{cm^{-1}}$ and $x_P = 1{\cdot}8$ per cent. (N_α was fixed at $367 \times 10\,\mathrm{cm^3\,mol^{-1}}$). Hence, we can suppose that the rise in μ_{eff} at the phase transition C_2C_3 is mainly caused by some changes in Co-ordination which lead to an increase in g-value and do not affect the small antiferromagnetic interactions in the proposed dimers. Most likely, the open lattice packing of the active form makes possible such a structural rearrangement in the C_3 phase, whereas this cannot occur in the more close packing of the inactive form. Due to lack of a proper relationship between the g-value (μ_{eff} at r.t.) and structural parameters for square-planar or octahedral coordinated Cobalt(II) compounds, it is impossible to predict from the magnetic data alone what kind of structural change leads to this increase in μ_{eff}.

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