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2D molecular square grid of Cobalt(II) with tridentate phenylglycinate and mandelate: structure and magnetism

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Abstract

The hydrothermal synthesis, single crystal X-ray structures and magnetic properties of two layered cobalt-carboxylate complexes, ${}^{2}_{\infty}[\mathrm{Co^{II}}(O_2C^*CH(OH)C_6H_5)_2]$ (**1**) and ${}^{2}_{\infty}[\mathrm{Co^{II}}(O_2C^*CH(NH_2)C_6H_5)_2]$ (**2**), where $O_2CCH(OH)C_6H_5$ is mandalate and $O_2CCH(NH_2)C_6H_5$ is phenylglycinate, are described. Pale pink crystals of **1** and **2** were obtained by the reaction of cobalt nitrate and the enantiomer-pure acids at 120 °C. In each case, the structure consists of stacks of quasi square-grid polymeric sheets consisting of carboxylato- bridges, M–O–C–O–M, and the presence of both D- and L-enantiomers of the ligands segregated on each face of the layer. The ligands exhibit both chelating and bridging functions with the carboxylate group adopting an *anti–anti* mode. The magnetic properties are characteristic of weakly interacting paramagnets where the moments are elevated by an important orbital contribution via spin-orbit coupling.

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1. Introduction

The design of polymeric coordination networks has advanced considerably due principally to the potential applications for sorption, selective catalysis, ion-exchange and also for their magnetic properties [1–3]. Amongst these systems, 2D layered compounds have a very special place [4,5]. Layered compounds have been known for a very long time and many of them have been exploited for their intercalation chemistry. Several structural topologies within the layers have been described including triangular-, hexagonal- and square-grid networks. Our ongoing interest in this area has focused on the development of novel layered magnetic compounds [6] for they belong to a special class amongst magnetic materials and are used as models for the understanding of (a) the presence of long range magnetic ordering, theoretically not possible for 2D-Heisenberg system but made possible by the presence of a weak dipolar through-space interaction and (b) the magnetic properties of multi-layer systems with different types of exchange mechanism. Examples of magnetic triangular lattice are those of hydroxides [6] or silicates [7]; those with hexagonal symmetry are oxalates [8,9] and metal-P_2S_6 [10] and for square-grid there are halide and oxide perovskites [11], thiocyanate [12], cyanides [13], dicyanamides [14] and carboxylates [15]. Here, we present two examples of layered compounds having M–O–C–O–M bridges where the bridge is made by the carboxylate groups of mandelic acid (α-hydroxyphenylacetic acid) or phenylglycine (α-amino-phenylacetic acid). The two acids were expected to also provide the additional property of optical activity.

A search through Chemical Abstracts for coordination complexes of cobalt with mandelic acid gave eight hits where the main interests were the characterisation of the molecular structure by infrared, circular dichroism, formation constants and thermal properties [16]. No characterisation of any crystal phase was reported. Similar search for phenylglycine of cobalt gave one hit reporting its complexation property in solution [17].

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2. Experimental

All chemicals of purity higher than 98% were purchased from Tokyo Kasei and Aldrich and were used without further purification.

2.1. Preparation of [Co($O_2CCH(OH)C_6H_5)_2$] (**1**) and [Co($O_2CCH(NH_2)C_6H_5)_2$] (**2**)

The synthesis of the two compounds was performed in exactly the same way in 120 ml capacity autoclave. In each case, $Co(NO_3)_2 \cdot 6H_2O$ (1.0 g, 0.0035 mol) was dissolved in distilled water (ca. 20 ml) and a solution of the acid, enantiomer-pure L-mandelic acid ($HO_2CCH(NH_2)C_6H_5$) (0.52 g, 0.0035 mol) or D-phenylglycine ($HO_2CCH(NH_2)$-C_6H_5) (0.52 g, 0.0035 mol), and NaOH (0.14 g, 0.0035 mol) in distilled water (ca. 20 ml) was added. The mixture was placed in the Teflon liner of the autoclave, sealed and heated to 120 °C for 1 day. It was then allowed to cool to room temperature. In both cases pale pink plates were obtained which were harvested, washed with water and acetone and allowed to dry in air.

2.2. X-ray crystallography and structure solution

The single crystals were selected and glued on the tip of glass fibers with epoxy resin. Their diffraction data were collected on a Bruker SMART APEX CCD area detector employing ω-scan mode at room temperature. The diffractometer is equipped with a graphite monochromated Mo Kα (0.7107 Å) radiation. The data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods and expanded using Fourier techniques [18]. The non-hydrogen atoms were refined anisotropically. The final cycle of the full-matrix least-squares refinement was based on the number of observed reflections and n variable parameters. They converged (large parameter shift was σ times its e.s.d.) with agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. No extinction corrections have been applied. Details of crystallographic data are collected in Table 1. The crystal data have been deposited at CCDC, Cambridge, UK and given the reference numbers CCDC 213444 and 213445.

Table 1
Crystallographic data for [Co($O_2CCH(OH)C_6H_5)_2$] (**1**) and [Co(O_2-$CCH(NH_2)C_6H_5)_2$] (**2**)

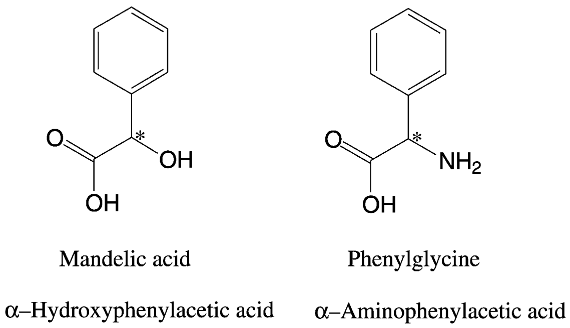
Complex	**1**	**2**
Empirical formula	$O_6C_{16}H_{12}Co$	$O_{24}C_{16}H_{16}CoN_2$
Formula weight	359.20	359.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	15.512(3)	15.478(2)
b (Å)	4.8857(9)	4.9948(6)
c (Å)	9.365(2)	9.457(1)
β (°)	99.979(3)	99.809(2)
V (Å^3)	699.0(2)	720.4(2)
Z	2	2
D_c (g cm^{-3})	1.706	1.656
μ (Mo Kα) (cm^{-1})	20.61	16.36
R, R_w	0.091, 0.144	0.097, 0.119
R_1	0.050	0.040

3. Results and discussions

As the interest in the area of coordination polymers is becoming more apparent by the number of interesting low dimensional and framework materials that are being synthesised [1], the research area is expanding in various directions and in particular, that where the ligands contain carboxylate groups. One is to functionalise the aromatic rings or alkyl chains to which the carboxylate group is attached with nitrogen donor groups [19], in particular, to provide further coordination capabilities for specific functions. Our present interest was to use ligands with a coordinating group on the α-carbon of acetic acid and also to choose those that have optical activity. Thus, in this work reactions were performed with Co(II) and two chiral mono-carboxylic acids, mandelic acid and phenylglycine (Scheme 1). The ligand contains either an –OH group or an $-NH_2$ group, respectively, on the α-carbon of acetic acid. In both cases, we choose the enantiomer pure starting materials for the reactions. However, the single crystal structure analyses revealed the formation of compounds containing racemic mixture of the two enantiomers, which presumably produced during the hydrothermal reactions. The lack of any circular dichroism in the UV–vis spectra of **1** and **2** dispersed in KBr disks confirms the presence of both enantiomers to produce non-chiral compounds. This is not so surprising since it is well known that racemisation of the ligands is favoured in the presence of bases [20].

3.1. Structure of [Co($O_2CCH(OH)C_6H_5)_2$] (**1**) and [Co($O_2CCH(NH_2)C_6H_5)_2$] (**2**)

The asymmetric unit contains one ligand and one half of cobalt atom in each case. A drawing of the asymmetric unit and the atomic numbering scheme is shown in Fig. 1. A summary of the crystal data of the two compounds is given in Table 1. The selected bond distances and angles of **1** and



Scheme 1.

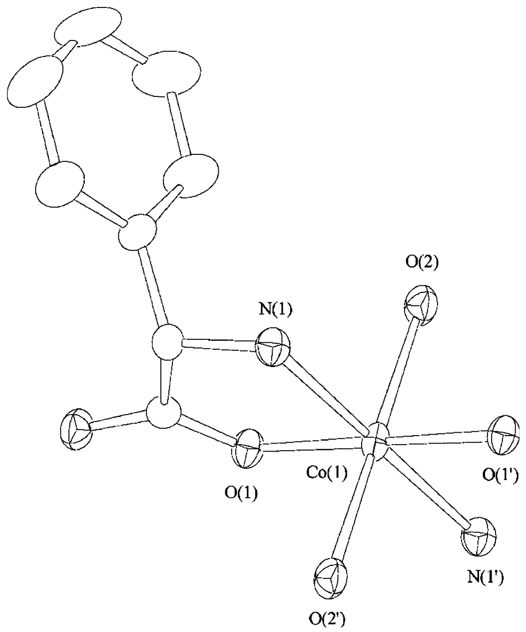


Fig. 1. Atomic numbering scheme for Co(phenylglycinate)$_2$ (**2**); the same scheme is adopted for Co(mandelate)$_2$ (**1**) by replacing N(1) by O(3).

2 are given in Tables 2 and 3, respectively. The common key feature of the structures is the stacking of square-grid layers of cobalt-oxygen separated by the phenyl rings of the ligands (Figs. 2 and 3). The layers are parallel to the *bc* plane separated by the ligands along the *a*-axis, giving interlayer distances of ca. 15.5 Å. The interlayer separation is very close to that found in $Co(H_2O)_2$(*trans*-cinnamate)$_2$ [21]. Each layer contains octahedral Co(II) ions connected by four equatorially coordinated O–C–O bridges of the carboxylate groups. Within the layer, the three distinct Co–Co distances are 4.89, 5.28 and 9.37 Å **1** and 4.99, 5.35 and 9.46 Å for **2**. Square arrangement of Co(II) ions was previously found in $Co(H_2O)_2L_n$ ($n = 1$: benzene 1,4-dicarboxylate or terephthalate and 4-carboxycinnamate, $n = 2$: *trans*-cinnamate) type compounds and Co(formate)$_2$(urea)$_2$ [22,23]. In contrast to the latter, **1** and **2** are severely distorted by compression along the *b*-axis and elongation along the *c*-axis. Consequently, the two short axes become non-equivalent in **1** and **2**. The shortest distances of **1** and **2** are very similar to those found in $Co(H_2O)_2L_n$. However, the area defined by the four nearest cobalt neighbours is 45.75 Å^2 for **1**, 47.23 Å^2 for **2** and lies between 46.92 and 47.73 Å^2 for $Co(H_2O)_2L_n$. This suggests that the grids are highly flexible but retain their planarity.

Table 2
Selected bond distances (Å) and angles (°) of [$Co(O_2CCH(OH)C_6H_5)_2$] (**1**)

Atom	Atom	Distance	
Co(1)	O(1)	2.048(2)	
Co(1)	O(2)	2.160(2)	
Co(1)	O(3)	2.114(2)	
Atom	Atom	Atom	Angle
O(1)	Co(1)	O(1′)	180.0
O(1)	Co(1)	O(2′)	97.42(7)
O(1)	Co(1)	O(3′)	101.60(7)
O(1)	Co(1)	O(2)	82.58(7)
O(2)	Co(1)	O(2′)	180.0
O(1)	Co(1)	O(3)	78.40(7)
O(2)	Co(1)	O(3)	90.08(7)
O(2′)	Co(1)	O(3)	89.92(7)
O(3)	Co(1)	O(3′)	180.0

Table 3
Selected bond distances (Å) and angles (°) of [$Co(O_2CCH(NH_2)C_6H_5)_2$] (**2**)

Atom	Atom	Distance	
Co(1)	O(1)	2.047(2)	
Co(1)	O(2)	2.247(2)	
Co(1)	N(1)	2.114(3)	
Atom	Atom	Atom	Angle
O(1)	Co(1)	O(1′)	180.0
O(1)	Co(1)	O(2′)	94.99(8)
O(1)	Co(1)	N(1′)	100.40(9)
O(1)	Co(1)	O(2)	85.01(8)
O(1)	Co(1)	N(1)	79.60(9)
O(2)	Co(1)	O(2′)	180.0
O(2)	Co(1)	N(1)	89.85(8)
O(2)	Co(1)	N(1′)	90.15(8)
N(1)	Co(1)	N(1′)	180.0

The cobalt ions exhibit octahedral geometry comprising four oxygen atoms of carboxylate groups and two oxygen atoms of –OH groups for **1** or two nitrogen atoms of $-NH_2$ groups for **2**. These O (OH) or N (NH_2) atoms coordinate in *trans*-positions. In contrast to the coordination of $Co(H_2O)_2L_n$ the additional coordinating site of the ligands occupy the sites of the water molecules. Consequently, the presence of the –OH or $-NH_2$ group results in the chemical formula CoL_2 (L = mandelate or phenylglycinate) without the need of coordinated water. The –OH and $-NH_2$ groups coordinate to Co(II) centers to give O–C–C–OH ($-NH_2$) five-membered chelate ring. The Co–O and Co–N are both normal. However, the bonding of the cobalt to the –OH or $-NH_2$ groups exerts severe distortion of the octahedra. The bond angles lie in the range 78.40(7) to 101.60(7)° and 79.60(9) to 100.40(9)° for **1** and **2**, respectively. Although, these distortions are present in the $Co(H_2O)_2L_n$ compounds, they are more pronounced for **1** and **2**. The structural difference between the two $Co(H_2O)_2L_n$ and CoL_2 is principally due to the small chelate angles of the ligands. The third coordination by the ligands through the additional group on the α-carbon exerts severe distortion on the carboxylate groups and consequently, it results in the compression of the squares compared to $Co(H_2O)_2L_n$.

We anticipated that the use of optically pure ligands may result in optically active coordination polymers as has been seen in some cases [24]. In fact, the racemisation of the ligand in the presence of a base, which is needed for the reactions, resulted in compounds having a racemic mixture

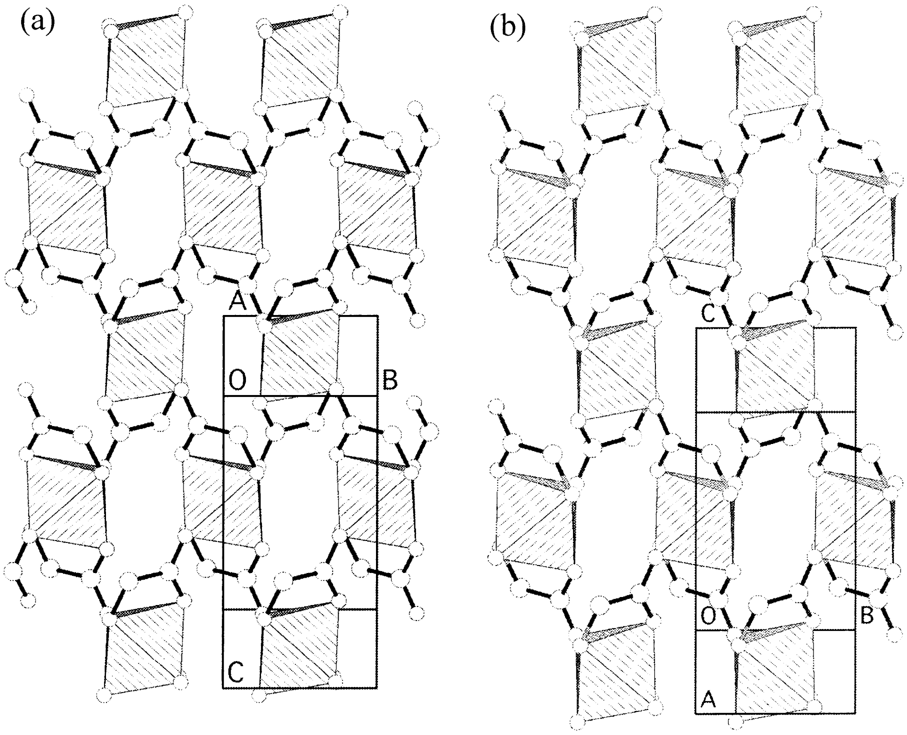


Fig. 2. View of the layer structures of (a) Co(mandelate)$_2$ (**1**) and (b) Co(phenylglycinate)$_2$ (**2**) showing the three coordination bonds of each ligand. The benzene rings are omitted for clarity.

of the two enantiomers (Fig. 4). Interestingly, within the space group of the crystals the two enantiomers are forcibly segregated on each side of the layer, respectively.

The mid-infrared spectra of the compounds measured by transmission in a KBr pellet display bands at 3255 cm^{-1} (OH), 1573 cm^{-1} (antisymmetric carboxylate stretching) and 1408 cm^{-1} (symmetric carboxylate stretching) for Co(mandelate)$_2$; 3358 and 3247 cm^{-1} (NH), 1566 cm^{-1} (antisymmetric carboxylate stretching) and 1395 cm^{-1} (symmetric carboxylate stretching) for Co(phenylglycinate)$_2$. The large difference between the antisymmetric and symmetric stretching modes of the carboxylate is in agreement with that expected for an *anti–anti* coordination mode [25].

The magnetic properties of the compounds were measured on polycrystalline samples by use of a SQUID (Quantum Design) magnetometer in the temperature range 2–300 K and field up to 5 T. The results are shown in Figs. 5 and 6. The absolute values and the temperature dependence of the moments, represented as the product of susceptibility and temperature, are typical for the presence of an orbital contribution for Co(II) [26]. The data above 100 K were fitted to the Curie–Weiss law with Curie constant 3.3 ± 0.2 cm^3 K mol^{-1} and Weiss temperature of -11.1 ± 0.1 K for **1** and -8.5 ± 0.3 K for **2**. These values are in good agreement with those expected for almost non-interacting Co(II). The Weiss constants are, however, less than that estimated (ca. -20 K) if a spin-orbit contribution is included for a perfect octahedral complex of cobalt(II), suggesting that the severe distortion of the octahedral may have resulted in a lower spin-orbit coupling [26]. However, a small but finite exchange interaction between neighbouring cobalt atoms cannot be excluded.

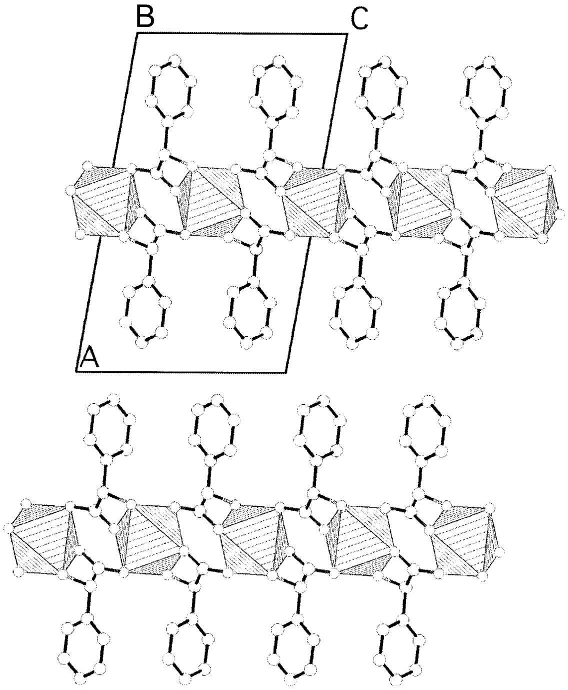


Fig. 3. View of the structure of Co(phenylglycinate)$_2$ showing the stacking of the layers along the *a*-axis. Note that there is no interleaving of the phenyl rings.

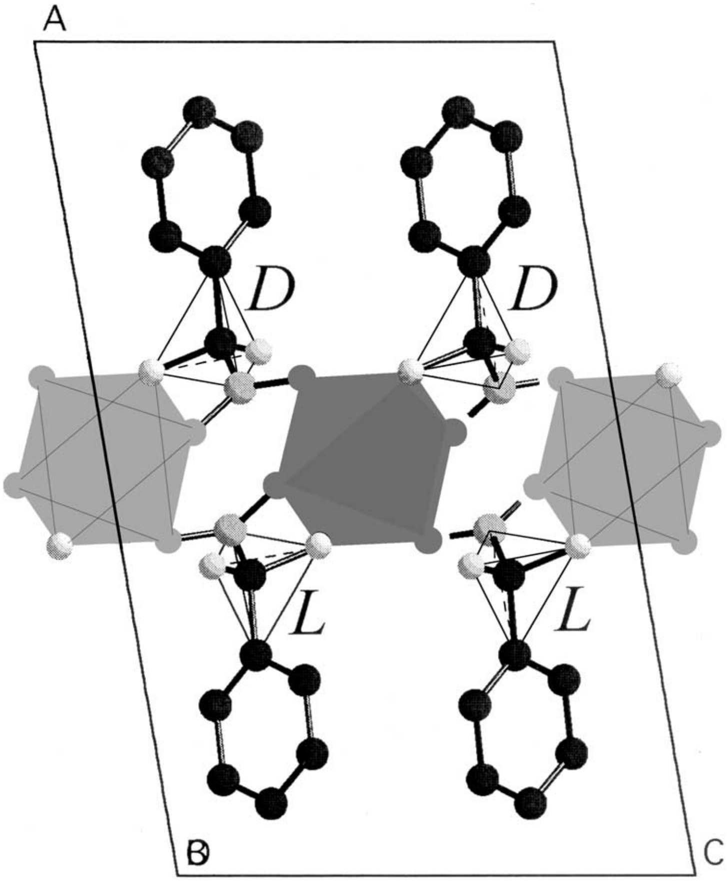


Fig. 4. View of the layer structure of Co(phenylglycinate)$_2$ highlighting the segregation of the enantiomers D and L on the opposite sides of the layer. The carboxy carbon atom is drawn in large grey ball, nitrogen and hydrogen in small light grey balls. The hardedness is shown by the tetrahedral coordination of the α carbon.

4. Conclusion

In summary, two new layered compounds have been identified in the hydrothermal reaction of Co(II) and mandelic acid or phenylglycine in alkaline media. Racemisation of the ligands occurred during the hydrothermal reaction results in the coordination of both enantiomers and they are segregated on the two faces of the layer by symmetry. The coordination of –OH or –NH_2 groups yield CoL_2 type compounds in which the same square-grid structure was found as in other $Co(H_2O)_2L_n$. The non-interacting moment on the cobalt atoms suggests that the O–C–O bridges are less effective for magnetic exchange [6,22].

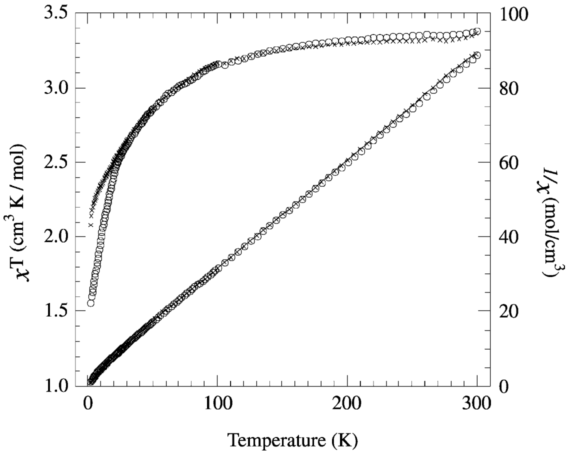


Fig. 5. Temperature dependence of the χT product and $1/\chi$ for Co(mandelate)$_2$ (circles) and Co(phenylglycinate)$_2$ (crosses).

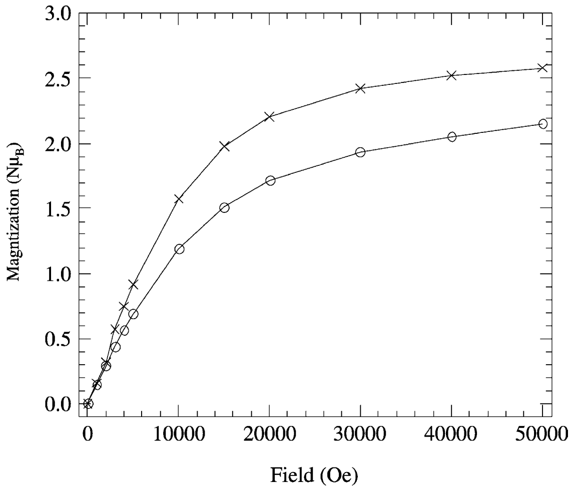


Fig. 6. Isothermal magnetisation of Co(mandelate)$_2$ (circles) and Co(phenylglycinate)$_2$ at 2 K. Lines are guides to the eyes.

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