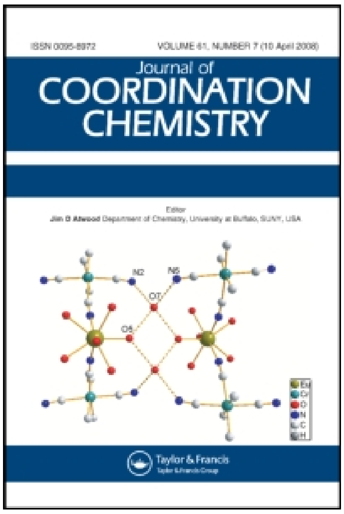

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X-ray structure and magnetochemical study on a Co(II) complex of 2-acetyl-1,3-indandione

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X-ray structure and magnetochemical study on a Co(II) complex of 2-acetyl-1,3-indandione

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An X-ray structure of a Co(II) complex of bidentate chelating 2-acetyl-1,3-indandione (2AID) is reported – $Co(2AID)_2(H_2O)_2 \cdot 2H_2O$. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The molecular structure shows distorted octahedral geometry of the metal center. The complex is characterized by EPR and magnetic measurements, which show high-spin electronic structure for the metal ion.

Keywords: Co(II) complex; X-ray structure; Magnetochemistry; EPR

1. Introduction

The physiological activity of 2-acetyl-1,3-indandione (2AID) and its derivatives is well documented [1, 2]. Although that 2AID belongs to the class of cyclic β-diketones, known for good chelation ability, there are only a few reports about metal complexes of this compound. Most date back to the 70's and the structural investigations are based on elemental analyses, IR and UV-Vis spectra only [3–7].

Recently we started systematic investigations on Cu(II), Zn(II) and newly synthesized Pb(II) and Cd(II) complexes of 2AID studied by NMR (in solution and solid state) and quantum chemical *ab initio* methods [8]. Moreover, X-ray structure, EPR and Mössbauer data of the Fe(III) complex of 2AID were reported [9].

Here we show X-ray data together with magnetochemical and EPR studies on a Co(II) complex of 2AID, which has been previously synthesized and a tetrahedral structure of the complex was falsely suggested [10].

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2. Experimental

2.1. *General*

All reagents and solvents used were of AR grade. The IR spectrum was recorded on a Perkin-Elmer FTIR-1600 spectrophotometer (KBr pellets). The low temperature magnetochemical measurements were performed on SQUID and VSM magnetometers. The data were corrected for diamagnetic contributions, estimated from Pascal constants. The EPR measurement at 5 K was obtained using a Varian E-9 spectrometer, equipped with an Oxford Instruments ESR9 helium flux cryostat at 9.366 GHz.

2.2. *Synthesis of a Co(II) complex*

Methanol solution of $Co(CH_3COO)_2 \cdot H_2O$ (0.5 mmol, 97.5 mg) is mixed with methanol solution of 2AID (1.0 mmol, 188.2 mg). Heating the reaction mixture to 50°C led to formation of an orange precipitate, which was filtered and dried over P_2O_5 for two weeks. Selected IR frequencies (KBr): $\nu = 3190(\text{br, w}), 1680(\text{m}), 1610(\text{s}), 1590(\text{s})\ \text{cm}^{-1}$.

2.3. *X-ray structure determination*

Single crystals from $[Co(C_{11}H_7O_3)_2(H_2O)_2] \cdot 2(H_2O)$ were obtained after recrystallization from acetonitrile. The data were collected at 100(2) K on an Xcalibur3 4 circle diffractometer using a graphite monochromator, Mo-Kα radiation, equipped with a low temperature device. Three standard reflections were monitored to control the stability of the crystal and the system revealed no intensity decay. The data set was corrected for Lorentz and polarization effects and absorption correction was made using the multi-scan method.

The structure was solved using direct methods with SIR97 software and refinement was carried out using the SHELXL-97 software package [11]. All non-hydrogen atoms were located from the initial solution or from subsequent electron density difference maps during the initial course of the refinement. After locating the non-hydrogen atoms the models were refined against F^2, first using isotropic and finally anisotropic thermal displacement parameters. The hydrogen atoms were treated with the riding method.

High anisotropic displacements were found for the oxygen atoms of solvent water, probably due to disorder or thermal motion. Water oxygen positions described with partial occupancy are O2w, O3w, and O4w.

More details about the structure and its refinement are given in table 1.

3. Results and discussion

It is well documented that 2AID exists in exocyclic enolic form stabilized by an intramolecular hydrogen bond [12, 13]. 2AID coordinates to a metal ion after deprotonation of the enolic group and is a bidentate ligand. The presence of a carbonyl group, which is not involved in the coordination, makes possible intermolecular interactions or even formation of polynuclear species.

Table 1. Crystal data and structure refinement details for $[Co(C_{11}H_7O_3)_2(H_2O)_2] \cdot 2H_2O$.

Empirical formula	$C_{22}H_{18}CoO_{10}$
Formula weight	501.29
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space Group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	7.4163(2)
b	15.2383(4)
c	18.5272(4)
α	90
β	93.914(1)
γ	90
Volume (Å^3)	2088.91(9)
Z	4
Calculated density (Mg m^{-3})	1.594
Absorption coefficient (mm^{-1})	0.881
F(000)	1028
Crystal size (mm^3)	$0.3 \times 0.3 \times 0.2$
Theta range for data collection (°)	3.84 to 30.49
Limiting indices	$-9 \le h \le 9$, $-21 \le k \le 21$, $-18 \le l \le 26$
Reflections collected/unique	15254/5579 [R(int) = 0.0515]
Completeness to $\theta = 30.49$	87.5%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5579/0/365
Goodness-of-fit on F^2	1.082
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0640$, $wR_2 = 0.0981$
R indices (all data)	$R_1 = 0.1297$, $wR_2 = 0.1477$

A non-charged Co(II) complex of 2AID has been isolated only when cobaltous acetate was used as starting salt. Orange prismatic crystals of the complex were obtained from acetonitrile solution after slow evaporation and studied by single crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. An ORTEP view of the resolved structure of $Co(2AID)_2(H_2O)_2$ and unit cell representation are given in figure 1.

Two deprotonated ligands and two waters are coordinated to the metal center, giving octahedral cobaltous ion surrounded by six oxygens. The oxygen atoms from 2AID lie in the equatorial plane on an average distance from the metal center of 2.064(5) Å. The maximum deviation from this value is 0.015(5) Å. Both ligand fragments are almost coplanar with the equatorial plane (dihedral angles 4.6(2)° and 13.5(2)°). The two water molecules are axially coordinated at slightly longer distances (2.129(6) Å and 2.116(6) Å for Co1–O2 and Co1–O1, respectively). The cobaltous ion is 0.013(2) Å above the equatorial plane. The O1–Co1–O2 plane forms an angle of 88.9(2)° with the equatorial plane.

Although the overall structure of the complex is an elongated octahedron, some trigonal distortions are present. The bond angles O–Co–O in the equatorial plane vary from 99.5(2) and 83.6(2)° for the angles outside the chelate rings, to 88.2(2) and 88.7(2)° for those inside the chelate rings. Moreover, the two oxygen atoms from the water molecules and the cobaltous ion do not lie on a line; the O1–Co1–O2 angle is 178.7(2)°. Selected distances and angles are listed in table 2.

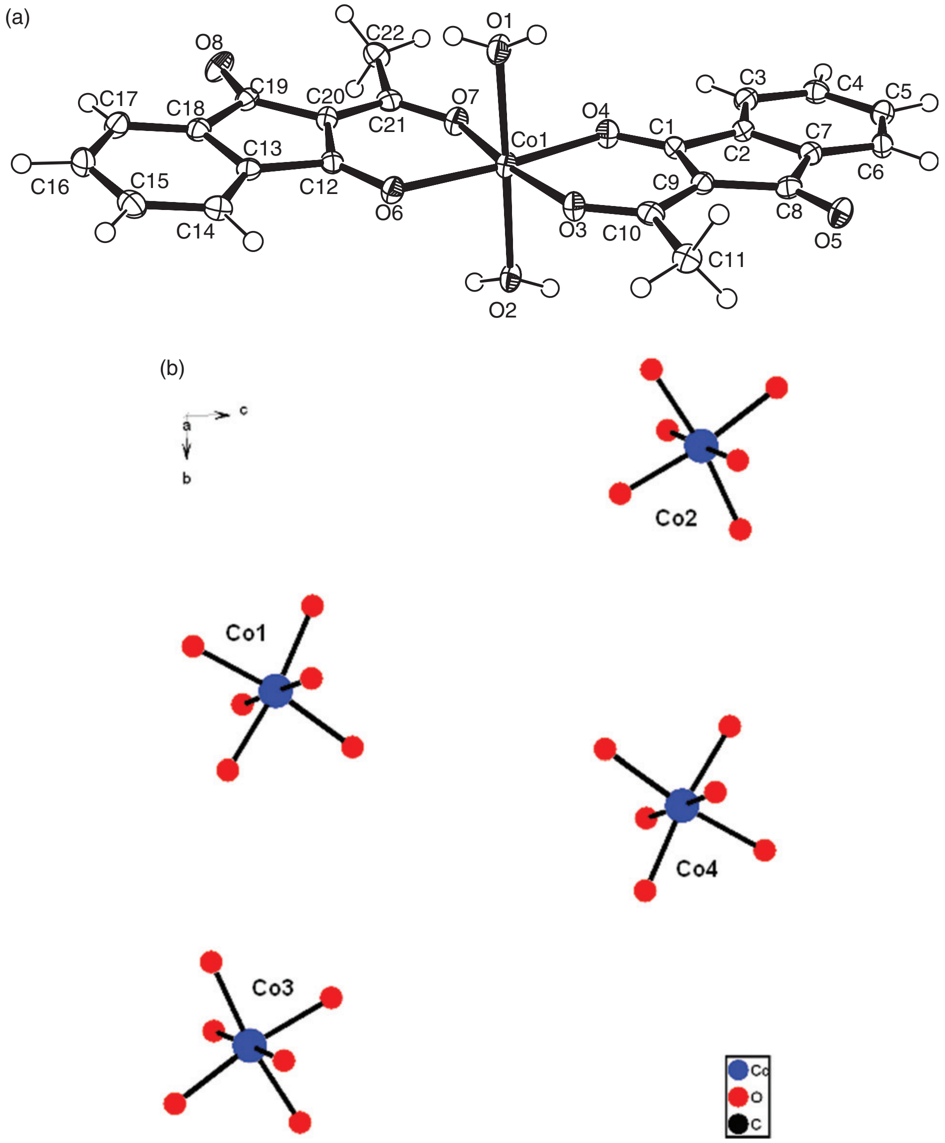

Figure 1. (a) ORTEP drawing of the single-crystal X-ray structure of Co(2AID)$_2$(H$_2$O)$_2$; (b) projection along *a* of the four Co(II) ions in the unit cell.

The unit cell contains four identical Co centers, which are related by the symmetry operations of the space group $P2_1/n$ [figure 1(b)]. Co1 is related to Co2 by a two-fold screw axis, as well as Co3 to Co4. Co1 and Co3 are related to Co4 and Co2, respectively, by inversion. The crystal lattice of the studied compound consists of a 3D network of Co(II) ions, with the closest intermetallic distances in the range 7.51–11.32 Å. Different views of the crystal packing are presented in figure 2. Additionally, disordered waters are incorporated in the space between the individual molecules.

Table 2. Selected bond lengths (Å) and angles (°) for $[Co(C_{11}H_7O_3)_2(H_2O)_2]\cdot 2(H_2O)$. For numbering of the atoms see figure 1.

Co(1)–O(2)	2.129(5)	O(3)–Co(1)–O(7)	172.2(2)
Co(1)–O(1)	2.116(6)	O(3)–Co(1)–O(4)	88.6(2)
Co(1)–O(4)	2.068(5)	O(3)–Co(1)–O(6)	98.8(2)
Co(1)–O(7)	2.054(5)	O(7)–Co(1)–O(4)	83.5(2)
Co(1)–O(6)	2.079(6)	O(7)–Co(1)–O(6)	88.9(2)
Co(1)–O(3)	2.053(5)	O(4)–Co(1)–O(6)	172.4(2)
O(5)–C(8)	1.237(8)	O(4)–Co(1)–C(9)	128.5(2)
O(4)–C(1)	1.244(8)	C(10)–O(3)–Co(1)	130.3(2)
O(7)–C(21)	1.259(8)	C(1)–O(4)–Co(1)	125.0(2)
O(6)–C(12)	1.245(8)	C(12)–O(6)–Co(1)	123.3(2)
C(9)–C(10)	1.428(9)	C(21)–O(7)–Co(1)	129.4(2)

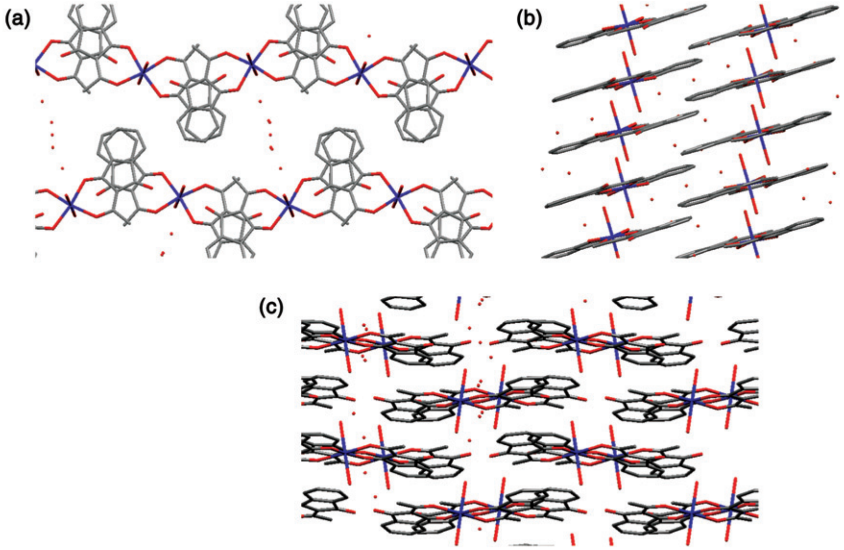

Figure 2. (a) View of the unit cell of $Co(2AID)_2(H_2O)_2$ along the *a* axis, (b) along the *b* axis, (c) along the *c* axis. Hydrogen atoms are omitted for clarity.

The temperature dependence of the magnetic susceptibility in the 300–2 K range is shown in figure 3 as χ_m^T *versus* T. The room temperature value of molar magnetic susceptibility ($\chi_m^T = 2.98\,\mathrm{emu\,K\,mol^{-1}}$) corresponds to effective magnetic moment equal to 4.88 BM. This value is in the 4.77–5.40 BM range corresponding to a high spin Co(II) ($S = 3/2$) in octahedral environment [14]. The low temperature magnetic data, however, may be understood if a system with effective spin $S = 1/2$ is assumed as a consequence of the splitting of the $^4T_{1g}$ level under the influence of spin-orbit coupling and crystal field effects. The magnetization as a function of applied magnetic field recorded at 2 K is given in figure 4. The saturation value of magnetization per mole measured at 6 kOe is 2.3 Nβ, N being Avogadro's number and β the electronic Bohr magneton, which differs from expected one for 3 unpaired electrons. From equation (1) it can be calculated that the *g*-factor of a system with effective spin 1/2 is equal to 4.6.

$$M_{\mathrm{sat}} = Ng\beta S \tag{1}$$

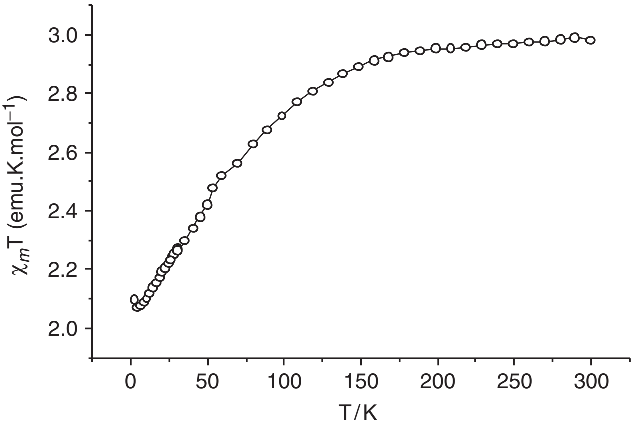

Figure 3. Molar magnetic susceptibility for $Co(2AID)_2(H_2O)_2$ presented as χ_m^T *vs.* T plot.

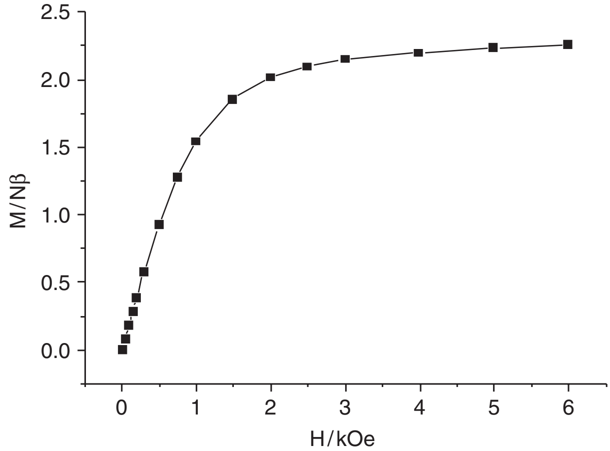

Figure 4. Magnetization (in units $N\beta$) of $Co(2AID)_2(H_2O)_2$ as a function of the applied magnetic field measured at 2 K.

The value of χ_m^T at 2 K is 2.07 emu K mol^{-1} (figure 3). It could be calculated from equation (2) [15] (where S is the total spin of the system and k is the Boltzmann constant) that a system with effective spin 1/2 has a g-factor equal to 4.7.

$$\chi_m^T = (Ng^2\beta^2/3k)S(S+1) \tag{2}$$

The X-band EPR spectrum of a powder sample of $Co(2AID)_2(H_2O)_2$ recorded at 5 K is presented in figure 5. The hyperfine structure expected for ^{59}Co isotope ($I=7/2$, 100% abundance) is not observed, presumably due to intermolecular exchange interactions. This spectrum is assigned to transitions between the states of the lowest Kramers doublet, having a highly anisotropic g-factor. The main feature of the spectrum is the very large magnetic anisotropy. Although the observed signals are rather broad, slight rhombicity might also be detected. Assuming effective spin $S'=1/2$ the following g-values are obtained: $g_1=9.5$, $g_2=2.80$, $g_3=2.00$. The average g-value,

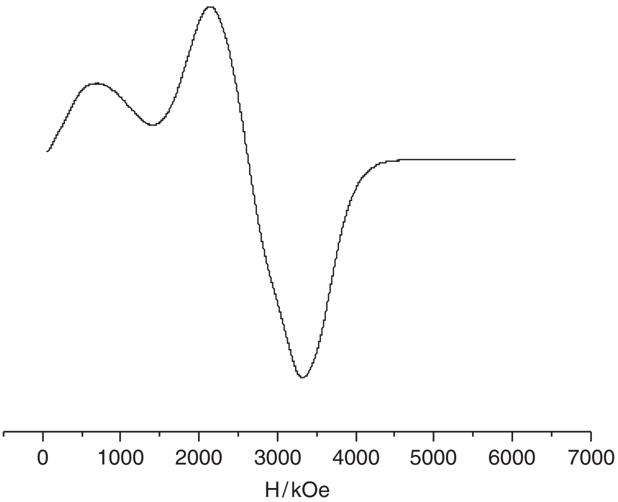

Figure 5. EPR spectrum of $Co(2AID)_2(H_2O)_2$ recorded at 9.366 GHz and 5 K.

$\langle g \rangle = 4.76$, is in agreement with the low temperature magnetic susceptibility data assuming effective spin of 1/2.

EPR spectra (on powdered sample and magnetically diluted single crystal) of a high-spin, low-symmetry Co(II) complex of acetylacetone ($Co(acac)_2(H_2O)_2$), having molecular structure similar to the Co(II) complex of 2AID, was reported by Bencini *et al.* [16], showing that the largest anisotropy in the g-value is observed when the axial ligands are water in comparison with N-containing ligands. This is explained with the largely anisotropic interactions of water molecules. More recently, other base adducts of $Co(acac)_2$ were studied by EPR spectroscopy and even larger anisotropy is observed (with estimated g-values $g_1 = 1.92$, $g_2 = 4.3$ and $g_3 = 10.7$) [17].

It should be noted that the observed EPR spectrum of the Co(II) complex of 2AID is not completely understood from current theories about magnetic anisotropy of low-symmetry, high-spin octahedral Co(II) complexes [14–16, 18]. Possible explanation assuming exchange interactions remains somehow improbable, since the structural data do not show relevant chemical paths connecting the metal sites that could efficiently transmit exchange interactions. The obtained powder spectrum can be considered as corresponding to isolated Co(II) ions, in which the resonance lines may be broadened by dipolar interactions. Clearly, further studies are needed, including single-crystal EPR measurements of magnetically dilute sample. Unfortunately, it was not possible to obtain a diamagnetic isostructural complex.

Supplementary data

Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data (CCDC 682226) can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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