Polyhedron 190 (2020) 114756

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, structure and magnetic property of a dinuclear cobalt(II/III) complex with a reduced Schiff base ligand



POLYHEDRON

Abhisek Banerjee^a, Santiago Herrero^b, Ángel Gutiérrez^b, Shouvik Chattopadhyay^{a,*}

^a Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700032, India ^b Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, Madrid 28040, Spain

ARTICLE INFO

Article history: Received 2 July 2020 Accepted 13 August 2020 Available online 18 August 2020

Keywords: Mixed valence Cobalt Dinuclear Reduced Schiff base Magnetic behaviour

ABSTRACT

A dinuclear mixed valence cobalt(II/III) complex, $[(N_3)Co^{II}L(\mu-CH_3COO)Co^{II}(N_3)]$ -CH₃OH with a N₂O₄ donor compartmental reduced Schiff base ligand, H₂L [(1,3-propanediyl)bis(iminomethylene)bis(6-ethoxyphenol)], has been synthesized and characterized by spectral and elemental analyses. Cobalt(III) is placed in the inner N₂O₂ compartment whereas cobalt(II) is present in the outer O₄ compartment of the ligand. Structure of the complex is confirmed by single crystal X-ray crystallography. The magnetic susceptibility measurement confirms that the complex belongs to localized class-I mixed valence system with isolated $S = 3/_2$ ion and shows Curie-Weiss paramagnetism.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Study of the magnetic properties of di and trinuclear transition metal complexes of Schiff bases has been an interesting research area in the field of materials science since a long time [1,2]. Easy synthetic routes, extensive stability and flexibility make the use of Schiff bases so much popular as ligand [3,4]. Recently, reduced Schiff bases have also been used to prepare transition metal complexes [5]. Different types of magnetic behaviors, e.g., ferromagnetic, antiferromagnetic, metamagnetic, single molecular magnetism (SMM), spin canting and spin flop have been observed in many such complexes of copper, nickel, iron and manganese [6-9]. Magnetism of dinuclear cobalt complexes, on the other hand, were less investigated probably because of the diamagnetic nature of low-spin cobalt(III) complexes [10-12]. Cobalt(II) complexes are suitable for magnetic study, but it is difficult to stabilize cobalt(II) in presence of strong field *N*-donor ligands. However recently a cobalt(II) SMM with only N-donor ligands has been reported in literature [13]. Cobalt may, however, form mixed valence cobalt(II/III) complexes via partial oxidation of cobalt(II) precursors and many di and trinuclear mixed valence cobalt(II/III) complexes were reported in literature [10-18]. Depending on the extent of electronic communication between the different metal sites, mixed valence compounds have been divided into three classes according to the Robin-Day classification viz. class-I, class-II and class-III [19]. The most renowned mixed valence cobalt complex is Co_3O_4 , a class-I type, in which cobalt(III) centers are octahedral and low spin, whereas cobalt(II) centers are tetrahedral and high spin [20]. Magnetic properties of these complexes were not studied in detail; rather their catalytic activities were investigated [10–12,16–18]. Few mixed valence cobalt complexes have been prepared with hydroxyl rich ligands and their magnetic properties were investigated [21,22].

In the present work, we have synthesized a mixed valence cobalt(II/III) complex with a N_2O_4 donor compartmental reduced Schiff base ligand. The complex has been characterized by spectral and elemental analyses. Its structure has been confirmed by single crystal X-ray diffraction analysis. The magnetic property of the complex has also be explored.

2. Experimental section

2.1. Materials

All chemicals used were purchased from Sigma-Aldrich and were of reagent grade. They were used without further purification.

Caution!!! Although no problems were encountered in this work, organic ligands in the presence of azide are potentially explosive. Only a small amount of the material (not more than 10 mmol) should be prepared and it should be handled with care.



^{*} Corresponding author. *E-mail address:* shouvik.chem@gmail.com (S. Chattopadhyay).

2.2. Synthesis

2.2.1. Synthesis of the reduced Schiff base ligand, H₂L [(1,3-propanediyl)bis(iminomethylene)bis(6-ethoxyphenol)]

20 mL methanol solution of 3-ethoxysalicylaldehyde (4 mmol, 0.66 g) and 1,3-propanediamine (2 mmol, 0.22 mL) was refluxed for 2 h to prepare a potential hexadentate N₂O₄ donor Schiff base ligand, H_2L^a {*N*,*N'-bis*(3-ethoxysalicylidene)propane-1,3-diamine}. Then the solution was cooled to 0 °C and solid sodium borohydride (4.00 mmol, 0.15 g) was added gently to the methanol solution with constant stirring. The resulting solution was acidified with glacial acetic acid (10 mL) and placed under reduced pressure in a rotary evaporator (~60 °C). The residue was dissolved in water (15 mL) and extracted with dichloromethane (15 mL) using a separating funnel. The ligand solution in dichloromethane was evaporated under reduced pressure and the ligand, H_2L , was extracted in methanol. The methanol was evaporated under reduced pressure to get the ligand, H_2L .

Yield: 0.46 g (~62.45%). Anal. Calc. for $C_{21}H_{30}N_2O_4$ (FW = 374.47): C, 67.3; H, 8.0; N, 7.5%. Found: C, 67.2; H, 7.9; N, 7.7%. ¹H NMR (DMSO-D6, 300 MHz) (ppm) δ : 1.360–1.211 [m, 6H, methyl CH₃ of ethoxy parts; 3.991–3.921 [m, 4H, methylene CH₂ of ethoxy parts], 3.797–3.775 [d, *J* = 6.6 Hz, 4H, methylene CH₂ of aldehyde part (adjacent to amine nitrogen)], 2.562–2.475 [m, 4H, methylene CH₂ (adjacent to amine nitrogen) of diamine], 1.605–1.560 [m, 2H, methylene CH₂ (central) of diamine part], 6.780–6.593 (m, 6H, aromatic CH).

2.2.2. Synthesis of the complex $[(N_3)Co^{III}L(\mu-CH_3COO)Co^{II}(N_3)]$ ·CH₃OH

A methanol solution (10 mL) of cobalt(II) acetate tetrahydrate (1.00 mmol, 0.25 g) was added to the reduced tetradentate Schiff base ligand, H_2L , (1.00 mmol, 0.37 g) with constant stirring for *ca*. 1 h. A solution of sodium azide (0.92 mmol, 0.06 g) in methanol/water solution (10 mL in a 4:1 ratio) was then added to it and stirring was continued for about 2 h more. Dark brown crystals appeared after 3–4 days on slow evaporation of the filtrate in an open atmosphere and X-ray quality single crystals were collected from the product.

Yield: 0.25 g (~75.24%, based on cobalt). Anal. Calc. for C₂₄H₃₅-Co₂N₈O₇ (FW = 665.46): C, 43.2; H, 5.2; N, 16.8%. Found: C, 43.3; H, 5.1; N, 16.9%. FT-IR (KBr, cm⁻¹): 3185 (ν_{N-H}), 2980–2895 (ν_{C-H}), 2026 (ν_{N3}), 2055 (ν_{N3}). UV–Vis, λ_{max} (nm), [ϵ_{max} (dm³ mol⁻¹ cm⁻¹)] (CH₃CN), 618 (6.25 × 10²), 365 (2.80 × 10³), 238 (1.5 × 10⁴).

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectrum in KBr (4500–500 cm⁻¹) was recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectrum in acetonitrile (200–800 nm) was recorded on a Perkin Elmer Lambda 35 UV–visible spectrophotometer. A Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device) magnetometer was used to measure the variable-temperature magnetic properties. ¹H NMR spectrum were recorded on a 300 MHz Bruker FT NMR spectrometer using DMSO-D6 as the solvent; chemical shifts (δ) are given in ppm.

2.4. X-ray crystallography

A suitable single crystal single crystal of the complex was used for data collection using a 'Bruker D8 QUEST area detector' diffractometer equipped with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using the SHELXL-18/1 package [23]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to nitrogen and oxygen atoms in the complex were located by difference Fourier maps and were kept at fixed positions. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [24]. A summary of the crystallographic data has been given in Table 1. Selected bond lengths and bond angles have been given in Table 2 and Table S1 (Supplementary information), respectively. It is to be mentioned here that there is a disorder in the position of one ethyl group attached to O(3) and two sets of positions {C(1), C(2) and C(25), C(26)} were refined with occupancies of x and 1 – x with x converging to 0.502(9).

3. Results and discussion

3.1. Synthesis

The potential hexadentate compartmental reduced Schiff base ligand, H_{2L} , was synthesised by facile condensation of 1,3-propanediamine with 3-ethoxysalicylaldehyde in 1:2 ratio followed by reduction with sodium borohydride in methanol under constant stirring at 0 °C [16–18]. This reduced Schiff base, H_{2L} , on reaction with cobalt(II) acetate tetrahydrate followed by the addition of sodium azide as co-ligand in methanol gave rise to the complex. The synthetic procedure of the complex has been shown in Scheme 1.

3.2. Structure description

X-ray crystal structure determination reveals that it crystallizes in the monoclinic space group, $P2_1/c$. Perspective view of the complex along with the selective atom labelling scheme has been shown in Fig. 1. H_2L , is a potential hexadentate compartmental reduced Schiff base having inner N₂O₂ and outer O₄ compartments with Co(1) center occupying the inner N₂O₂ cavity and Co(2) occupying the outer O₄ cavity. This is an example of a mixed valence complex where cobalt centers in the neutral dinuclear core are of different oxidation states i.e. +3 and +2, and this assignment can be confirmed by total charge balance considerations, interatomic distances of Co-N and Co-O and BVS (Bond valence sum) calculations [25–30]. The relative interatomic distances from cobalt(III)

Table 1	
Crystal data and refinement details of the comple	x.

	-
Formula	$C_{24}H_{35}Co_2N_8O_7$
Formula Weight	665.46
Crystal System	Monoclinic
Space group	P21/c
a(Å)	15.705(6)
b(Å)	9.114(3)
c(Å)	19.934(7)
β(°)	91.998(2)
$V(Å^3)$	2851.87(3)
Z	4
$d_{(calc)}$ [g cm ⁻³]	1.550
$\mu [{\rm mm}^{-1}]$	1.221
F(000)	1380
Total Reflections	48,470
Unique Reflections	6596
Observed data $[I > 2 \sigma(I)]$	5584
R(int)	0.030
*R1, [#] wR2 (all data)	0.0401, 0.0881
*R1, $^{\#}$ wR2 ([$I > 2 \sigma(I)$]	0.0317, 0.0837
Residual Electron Density (eÅ ⁻³)	0.489, -0.416

* $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and ${}^{\#}wR2 = \Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)^{1/2}$.

 Table 2

 Selected Bond lengths (Å) of the complex.

Co(1)-O(1)	1.946(12)
Co(1)-O(2)	1.958(13)
Co(1)-O(5)	1.929(12)
Co(1)-N(1)	1.986(1)
Co(1)-N(2)	1.978(1)
Co(1)-N(3)	1.922(2)
Co(2)-O(1)	2.027(13)
Co(2)-O(2)	2.024(13)
Co(2)-O(3)	2.284(1)
Co(2)-O(4)	2.314(3)
Co(2)-O(6)	2.063(14)
Co(2)-N(4)	1.997(3)

center, Co(1) (30, 3 N) lie in the range 1.920–1.986 Å, while those from cobalt(II) center, Co(2) (50, 1 N) are in the range 1.997-2.310 Å. In this complex, both cobalt centers adopt distorted octahedral geometry. The geometry of cobalt(II) is actually in between octahedral and trigonal prism (as could be identified from SHAPE analysis) [31]. The cobalt(III) center, Co(1), is coordinated by two amine nitrogen atoms, N(1) and N(2) and two phenoxy oxygen atoms, O(1) and O(2), of the deprotonated reduced Schiff base which constitute the equatorial plane. The fifth coordination site is filled by a nitrogen atom, N(3), of terminal azide, whereas an oxygen atom, O(5), of the bridging acetate moiety coordinates at the sixth site. Similarly for cobalt(II) center, Co(2), the equatorial plane consists of four oxygen atoms [two phenoxy oxygen atoms, O(1) and O(2), and two ethoxy oxygen atoms, O(3) and O(4)]. A nitrogen atom, N(4), of another terminal azide coordinates at the fifth site whereas the sixth coordination is filled by an oxygen atom, O(6), of the bridging acetate moiety (given in Table S1, Supplementary Information), which are being slightly deviated from the ideal values of 90° for the cis angles and 180° for the trans angles. The intramolecular separation between Co(1) and Co(2) is obtained as 2.980(5) Å. The distance is not satisfactorily short to infer any metal-metal bonding [16,32,33]. The saturated six membered chelate ring, Co(1)-N(1)-C(10)-C(11)-C(12)-N(2), represents a half chair conformation with puckering parameters [34], q(2) = 0.553(3) Å, $\phi = 184.5(8)^{\circ}$.

3.3. BVS calculation

The bond valence sum (BVS) calculations were performed to calculate the oxidation state of cobalt centers in the prepared complex. The results are in good agreement for confirming the existence of mixed valence states of cobalt in the complex. The BVS values are calculated as 3.04 and 2.01 for the Co(1) and Co(2) centers. Thus this bond valence sum calculative strategy strongly supports the assignment of mixed valence states of cobalt (+3 and +2) in the complex.



Fig. 1. Perspective view of the complex with selective atom labelling scheme. Non coordinated methanol molecule and hydrogen atoms have been omitted for clarity. Only one disorder position of the ethoxy side arm is shown.

3.4. Supramoloecular interactions

Two hydrogen atoms, H(1) and H(2), available in the ligand part are efficient for hydrogen bonding. Of these, H(1), attached to an amine nitrogen atom, N(1), is hydrogen bonded with a symmetry related oxygen atom, O(7)^a, of the solvent methanol molecule {symmetry transformation ^a = x,1 + y,z}; and H(2), attached to an amine nitrogen atom, N(2), is hydrogen bonded with the symmetry related azide nitrogen atom, N(8)^a, {symmetry transformation ^a = x,1 + y,z} of the neighbouring molecule. The azide nitrogen atom, N(4), is involved in hydrogen bonding interaction with the symmetry related hydrogen atom, H(7)^a, attached to an oxygen atom, O(7)^a, {symmetry transformation ^a = x,1 + y,z} of the neighbouring solvent methanol molecule. All these interactions led to the construction of a chain like structure (Fig. 2). The details of hydrogen bonding interactions have been given in Table 3.

In addition, C—H… π interaction is also prevalent in the complex. The hydrogen atom, H(12A), attached to carbon atom, C(12), is involved in inter-molecular C—H… π interaction with symmetry related (symmetry transformation ^b = 1-x,1/2 + y,1/2-z) phenyl ring, [C(14)-C(15)-C(16)-C(17)-C(18)-C(19)] (Fig. 3). The details of these C—H… π interactions have been shown in Table 4.

3.5. Hirshfeld surface analyses

Hirshfeld surfaces [35–37] and the 2D-fingerprint [38–40] plots of the complex were calculated by using Crystal Explorer software





Fig. 2. Perspective view of one dimensional chain through hydrogen bonding interaction in the complex. Only the relevant hydrogen atoms have been shown for clarity. Symmetry transformation: $a = x_1 + y_2$.

Table 3

Hydrogen bond distances (Å) and angles (°) for the complex.

D–H…A	D-H	Н…А	D…A	∠D-H…A	Symmetry transformation
$N(1)-H(1)\cdots O(7)^{a}$	0.88(2)	2.15(3)	2.998(2)	161(2)	^a = x,1 + y,z.
$N(2)-H(2)\cdots N(8)^{a}$	0.85(2)	2.46 (2)	3.270(3)	161(4)	
$O(7)-H(7)\cdots N(4)$	0.87(3)	2.04(3)	2.899(3)	175(3)	

D = donor; H = hydrogen; A = acceptor.



Fig. 3. Perspective view of the supra-molecular dimer formed by inter-molecular C–H··· π interactions with selective atom labelling scheme. Only relevant atoms have been shown in the figure. Symmetry transformation: ^b = 1-x,1/2 + y,1/2-z.

Table 4

Geometric features (distances in Å and angles in °) of the C–H $\dots\pi$ interactions obtained for the complex.

C—H…Cg(ring)	H…Cg(Å)	C—H…Cg	C…Cg (Å)	Symmetry transformation
C(12)-H(12A)···Cg(9) ^b	2.55	159	3.467(2)	^b = $1-x,1/2 + y,1/2-z$.

Cg(9) = Center of gravity of the ring [C(14)- C(15)-C(16)-C(17)-C(18)-C(19)].

[41]. Hirshfeld surface analysis has been explored in order to enhance the significance of the nature of the interactions between molecules in crystal lattice. The Hirshfeld surfaces have been mapped over d_{norm} (range -0.1 Å to 1.5 Å) shape index and curvedness (Fig. 4). Graphical plots of the molecular Hirshfeld surfaces mapped with d_{norm} used a red-white-blue colour scheme, where red highlights shorter contacts, white is used for contacts around the Van der Walls separation, and blue is for longer contacts. The intense circular depressions (deep red) seen on the surfaces indicates the hydrogen bonding contacts. The small extent of area and light colour on the surface indicates weaker and longer contact

other than hydrogen bonds. Thus Hirshfeld surface analysis serves as a powerful tool by which the intermolecular interactions of the complex have been quantified.

Two-dimensional fingerprint plots (Fig. 5) obtained from Hirshfeld surface analysis may also be useful in order to get quantitative information about the individual contribution of such supramolecular interactions in the crystal packing. Intermolecular interactions appear as distinct spikes in this plot. Complementary regions are observable in the two-dimensional fingerprint plots where one molecule act as donor ($d_e > d_i$) and the other as an acceptor ($d_e < d_i$). In the fingerprint plots the most dominant interactions have been



Fig. 4. Hirshfeld surfaces mapped with dnorm (left), shape index (middle) and curvedness (right) for the complex.



Fig. 5. Fingerprint plot: Full (a), resolved into H···C/C···H (b), H···N/N···H (c) and H···O/O···H (d) contacts contributed to the total Hirshfeld Surface area of the complex.

observed for N···H/H···N contacts i.e. 27.3% of the total Hirshfeld surface followed by C···H/H···C contacts with contribution of 14.0% of the total Hirshfeld surface. The contribution of interactions coming from O···H contacts are comparatively less i.e. 5.9%.

3.6. Magnetic measurements

The magnetic susceptibility of the complex has been measured in the temperature range of 2–300 K under a constant magnetic field of 1 T. The χT vs. *T* plot of the data also show these features (Fig. 6), with a room temperature value of 2.84 cm³ K mol⁻¹ that remains approximately constant on cooling up to 50 K. This value corresponds to a magnetic moment of 4.77 β , higher than the theoretical value for three unpaired electrons (3.88 β), but consistent with the usual values for isolated cobalt(II) ions [42], where the spin–orbit coupling renders values of 4.3–5.2 β . On lowering the temperature, the χT value decreases to a minimum value of 1.75 cm³ K mol⁻¹ at 2 K that corresponds to a magnetic moment of 3.75 β , in the range for a spin only magnetic moment in a high spin d^7 ion. This behaviour is compatible with a Curie-Weiss paramagnet, as shown in Fig. 7. On this basis the plot of χ^{-1} versus temperature yields a straight line with slope 0.3559(5) mol cm⁻³ K⁻¹ and intercept -0.19(9) K, R² = 0.9998. These values correspond to an average magnetic moment of 4.74(2) β , supporting the expected behaviour of isolated $S = {}^{3}/_{2}$ ions. This plot is compatible with a small spin–orbit coupling and/or a zero field splitting contribution, since the cobalt(II) environment is very regular with the two axial and two equatorial bond distances close to 2 Å, while the other two



Fig. 6. Temperature dependence of χT . The solid line represents the best fitting using the parameters described in the text.



Fig. 7. Plot of the inverse of susceptibility vs. temperature. The solid line represents the fitting of the data with the parameters reported in the text. The inset shows the temperature variation of the susceptibility and the corresponding fitting.

equatorial distances of around 2.2 Å can be mainly attributed to the distortion induced by the steric requirements of the ethoxy groups, more than to the influence of the metal ion configuration [43–46]. To account for these contributions the experimental data in Fig. 6 were fitted using PHI [47]. The Hamiltonian used in the fitting process corresponds to the sum of the Curie behaviour for the isolated $S = {}^{3}/_{2}$ plus a zero field splitting term: $H = g \cdot \beta \cdot S + D \cdot S_{z}^{2}$, where β is the Bohr magneton and D the zero field splitting paremeter. The best-fitted values were g = 2.39(1) and |D| = 5.3(1) cm⁻¹, with R² = 0.9991. The zero field splitting parameter appears in the usual range for slightly distorted octahedral cobalt (II) ions [21,48–50].

3.7. IR, electronic and NMR spectra

The IR and electronic spectra are in good agreement with the crystal structure of the complex. A moderately sharp band at 3185 cm^{-1} has been observed in the IR spectrum. This band is assigned to the N–H stretching vibration [51], confirming the fact



Scheme 2. Different types of protons of the ligand, H_2L appeared in ¹H NMR spectrum.

that the imine group of the Schiff base is reduced. The bands corresponding to alkyl C–H stretching occur in the range of 2990–2895 cm⁻¹ has been noticed in the IR spectrum of the complex. Most often metal-carboxylates show two absorption bands in the IR spectrum around 1413 and 1556 cm⁻¹ due to symmetric and anti-symmetric stretching vibrations, respectively [52,53]. In the current case, strong and sharp absorption bands at 1416 and 1560 cm⁻¹ have been observed which are attributed to symmetric and antisymmetric stretching vibrations of the carboxylate groups respectively [54]. A very strong band is obtained (which is bifurcated at 2026 cm⁻¹ and 2055 cm⁻¹) for azide groups [17]. IR spectrum of the complex has been provided in the Fig. S1 (Supplementary Information).

An intense absorption band at 365 nm may be assigned as charge transfer transitions from the coordinated ligand to the cobalt(III) center (LMCT) [55]. A broad absorption bands at 618 nm may be attributed to one of the two expected transitions $({}^{1}A_{1g} \rightarrow {}^{1}T_{1g} \text{ and } {}^{1}A_{1g} \rightarrow {}^{1}T_{2g})$ for any low-spin cobalt(III) in distorted octahedral geometry [17]. However, this band may also be considered as d-d transition band of cobalt(II) center [31]. However, any other bands originating from d-d transition is obscured by the high intensed LMCT transition [56]. High energy absorption band around 238 nm may be assigned to intra ligand π - π * transition [57]. Electronic spectrum of the complex has been given in the Fig. S2 (Supplementary Information). The complex does not exhibit any IVCT band on the time scale of the electronic transition, and this justifies that the complex essentially belongs to class-I localised mixed valence complex [58,59].

Scheme 2 refers to the assignment of different types of protons of the ligand, H_2L , found in ¹H NMR spectrum. In the ¹H NMR spectrum of the ligand, a multiplet peak for the methyl protons [a + b] of the ethoxy part of 3-ethoxysalicylaldehyde moiety have been noticed in the range 1.360–1.211 ppm. Signals for the aromatic protons of the 3-ethoxysalicylaldehyde moiety have been observed as a multiplet in the range 6.780–6.593 ppm. The benzyl protons [HNCH₂(e) + HNCH₂(f)] appear as doublet at 3.797 and 3.775 ppm. Signals for three different kind of methylene protons [OCH₂(c) + OCH₂(d)], [HNCH₂ (g) + HNCH₂ (h)] and [CH₂ (i)] present in the ligand appear as multiplet in the range 3.991–3.921 ppm, 2.562–2.475 ppm and 1.605–1.560 ppm respectively.

4. Conclusion

In the present work, we have reported the synthesis, structure and magnetic property of a dinuclear mixed valence cobalt(II/III) complex. Cobalt(III) is essentially low-spin in the complex and therefore does not contribute any magnetic moment due to the absence of unpaired electron in it. The room temperature magnetic moment of the complex is 4.77 β , which is although considerably higher than the theoretical value for three unpaired electrons (3.88 β), but this value is not unusual for a cobalt(II) complex due to the presence of spin-orbit coupling. The geometry of cobalt(II) is severely distorted from octahedral geometry. The variable temperature magnetic susceptibility data were fitted using the program PHI and the best-fitted values were g = 2.22 and |D|= 8.6 cm^{-1} . With the coordination geometry of the cobalt(II) and the D value, it is likely that the complex may exhibit SMM behavior (or at least field induced SMM behavior). We are currently trying to prepare a series of complexes of this type and will try to check their potential application as SMM. The work is in progress to improve the vield of the reaction and to develop more systems based on this strategy to generalize the concept.

Author contribution

Abhisek Banerjee: He synthesized the complex and characterized it by spectral and elemental analysis and performed all necessary works.

Santiago Herrero and Ángel Gutiérrez: They jointly performed the magnetic study of the complex.

Shouvik Chattopadhyay: He is the Principal Investigator of the project. He is also the corresponding author.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

A. B. thanks the UGC, India, for awarding a Junior Research Fellowship. S. H. thanks the Comunidad de Madrid (project B2017/ BMD-3770). S. C wishes to thank the RUSA 2.0 program of the Government of India, operating at Jadavpur University under which they each received "Research Support to Faculty Members" for Research Thrust Areas "Research in Advance Materials"; Sanction Ref. no. R-11/755/19 dated 27.06.2019.

Appendix A. Supplementary data

Supplementary information (SI) available: Hirshfeld Surface Analysis, Table S1 and Figures from S1-S2. CCDC 1832082 contains the supplementary crystallographic data for the complex. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114756.

References

- P. Bhowmik, H.P. Nayak, M. Corbella, N. Aliaga-Alcalde, S. Chattopadhyay, Dalton Trans. 40 (2011) 7916.
- [2] S. Jana, B.K. Shaw, P. Bhowmik, K. Harms, M.G.B. Drew, S. Chattopadhyay, S.K. Saha, Inorg. Chem. 53 (2014) 8723.
- [3] W. Qin, S. Long, M. Panunzio, S. Biondi, Molecules 18 (2013) 12264.
- [4] A. Elmali, M. Kabak, Y. Elerman, J. Mol. Struct. 477 (2000) 151.
- [5] S. Mirdya, M.G.B. Drew, A.K. Chandra, A. Banerjee, A. Frontera, S. Chattopadhyay, Polyhedron 179 (2020) 114374.
- [6] A. Bhattacharyya, B.N. Ghosh, S. Herrero, K. Rissanen, R.J. Aparicio, S. Chattopadhyay, Dalton Trans. 44 (2015) 493.
- [7] X.-Y. Wang, L. Wang, Z.-M. Wang, G. Su, S. Gao, Chem. Mater. 17 (2005) 6369.

- [8] S. Naiya, S. Biswas, M.G.B. Drew, C.J. Gómez-García, A. Ghosh, Inorg. Chem. 51 (2012) 5332.
- [9] T. Basak, K. Ghosh, C.J. Gómez-García, S. Chattopadhyay, Polyhedron 146 (2018) 42.
- [10] S. Majumder, S. Mondal, P. Lemoineb, S. Mohanta, Dalton Trans. 42 (2013) 4561.
- [11] R. Modak, Y. Sikdar, S. Mandal, S. Goswami, Inorg. Chem. Commun. 37 (2013) 193.
- [12] S.K. Dey, A. Mukherjee, New J. Chem. 38 (2014) 4985.
 [13] K. Ghosh, K. Harms, A. Bauza, A. Frontera, S. Chattopadhyay, CrystEngComm 20 (2018) 7281.
- [14] J. Luo, N.P. Rath, L.M. Mirica, Inorg. Chem. 6152 (2011) 50.
- [15] S. Chattopadhyay, G. Bocelli, A. Musatti, A. Ghosh, Inorg. Chem. Commun. 9 (2006) 1053.
- [16] A. Hazari, L.K. Das, R.M. Kadam, A. Bauzá, A. Frontera, A. Ghosh, Dalton Trans. 44 (2015) 3862.
- [17] A. Banerjee, S. Chattopadhyay, Polyhedron 177 (2020) 114290.
- [18] A. Hazari, A. Das, P. Mahapatra, A. Ghosh, Polyhedron 134 (2017) 99.
- [19] P. Day, M.B. Robin, Philos. Trans. R. Soc. A 5 (2008) 247.
- [20] K.P. Reddy, R. Jain, M.K. Ghosalya, C.S. Gopinath, J. Phys. Chem. C 121 (2017) 21472.
- [21] V. Chandrasekhar, A. Dey, A.J. Mota, E. Colacio, Inorg. Chem. 52 (2013) 4554.
- [22] S. Manna, A. Bhunia, S. Mistri, J. Vallejo, E. Zangrando, H. Puschmann, J. Cano, S.
- C. Manna, Eur. J. Inorg. Chem. (2017) 2585. [23] G.M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem. 71 (2015) 3.
- [24] G.M. Sheldrick, SADABS, V2014/5, Software for Empirical Absorption Correction, University of Göttingen, Institute fur Anorganische Chemieder Universitat, Gottingen, Germany, 1999–2003.
- [25] N.E. Brese, M. O'Keeffe, Acta Crystallogr. B 47 (1991) 192.
- [26] I.D. Brown, D. Altermatt, Acta Crystallogr. B 41 (1985) 244.
- [27] M. O'Keeffe, N.E. Brese, J. Am. Chem. Soc. 113 (1991) 3226.
- [28] H.H. Thorp, Inorg. Chem. 31 (1992) 1585.
- [29] G.J. Palenik, Inorg. Chem. 36 (1997) 122.
- [30] R.M. Wood, G.J. Palenik, Inorg. Chem. 37 (1998) 4149.
- [31] S. Alvarez, D. Avnir, M. Llunell, M. Pinsky, New J. Chem. 26 (2002) 996.
- [32] K.C. Mondal, P.P. Samuel, H.W. Roesky, E. Carl, R. Herbst-Irmer, D. Stalke, B. Schwederski, W. Kaim, L. Ungur, L.F. Chibotaru, M. Hermann, G. Frenkin, J. Am. Chem. Soc. 136 (2014) 1770.
- [33] N.M. Boyle, A.C. Coleman, C. Long, K.L. Ronayne, W.R. Browne, B.L. Feringa, M.T. Pryce, Inorg. Chem. 49 (2010) 10214.
- [34] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
- [35] M.A. Spackman, D. Jayatilaka, Cryst. Eng. Comm. 11 (2009) 19.
- [36] F.L. Hirshfeld, Theor. Chim. Acta 44 (1977) 129.
- [37] H.F. Clausen, M.S. Chevallier, M.A. Spackman, B.B. Iversen, New J. Chem. 34 (2010) 193.
- [38] A.L. Rohl, M. Moret, W. Kaminsky, K. Claborn, J.J. McKinnon, B. Kahr, Cryst. Growth Des. 8 (2008) 4517.
- [39] A. Parkin, G. Barr, W. Dong, C.J. Gilmore, D. Jayatilaka, J.J. McKinnon, M.A. Spackman, C.C. Wilson, Cryst. Eng. Comm. 9 (2007) 648.
- [40] M.A. Spackman, J.J. McKinnon, Cryst. Eng. Comm. 4 (2002) 378.
- [41] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, D. Jayatilaka, M.A. Spackman, Crystal Explorer 2.1, University of Western Australia, 2005-2007, http:// hirshfeldsurfacenet/CrystalExplorer/crystal_explorer@theochem.uwa.edu.au.
 [42] C.I. O'Connor, Progr. Inorg. Chem. 29 (1982) 204.
- [43] S. Akine, T. Nabeshima, Heteroat, Chem. 25 (2014) 410.
- [44] A. Biswas, L. Mandal, S. Mondal, C.R. Lucas, S. Mohanta, CrystEngComm 15
- (2013) 5888. [45] D.G. Branzea, A.M. Madalan, S. Ciattini, N. Avarvari, A. Caneschi, M. Andruh,
- New J. Chem. 34 (2010) 2479.[46] D.G. Branzea, A. Guerri, O. Fabelo, C. Ruiz-Perez, L.-M. Chamoreau, C. Sangregorio, A. Caneschi, M. Andruh, Cryst. Growth Des. 8 (2008) 941.
- [47] N.F. Chilton, R.P. Anderson, L.D. Turner, A. Soncini, K.S. Murray, J. Comput. Chem. 34 (2013) 1164.
- [48] R.L. Carlin, Magnetochemistry, Springer, Berlin, 1986.
- [49] R. Boca, Coord. Chem. Rev. 248 (2004) 757.
- [50] M. Murrie, Chem. Soc. Rev. 39 (2010) 1986.
- [51] S. Chattopadhyay, M.S. Ray, S. Chaudhuri, G. Mukhopadhyay, G. Bocelli, A. Cantoni, A. Ghosh, Inorg. Chim. Acta 359 (2006) 1367.
- [52] A.K. Sharma, F. Lloret, R. Mukherjee, Inorg. Chem. 52 (2013) 4825.
- [53] B. Cristóvão, B. Miroslaw, J. Kłak, M. Rams, Polyhedron 85 (2015) 697.
- [54] A. Banerjee, S. Banerjee, C.J. Gomez García, S. Benmansour, S. Chattopadhyay, ACS Omega 4 (2019) 20634.
- [55] M. Galini, M. Salehi, M. Kubicki, A. Amiri, A. Khaleghian, Inorg. Chim. Acta 461 (2017) 167.
- [56] S. Chattopadhyay, M.G.B. Drew, A. Ghosh, Eur. J. Inorg. Chem. (2008) 1693.
 [57] A.H. Kianfar, W.A.K. Mahmood, M. Dinari, M.H. Azarian, F.Z. Khafri,
- Spectrochim. Acta, Part A 127 (2014) 422.
- [58] S. Barlow, Inorg. Chem. 40 (2001) 7047.
- [59] T.L. Gianetti, G. Nocton, S.G. Minasian, N. Kaltsoyannis, A.L.D. Kilcoyne, S.A. Kozimor, D.K. Shuh, T. Tyliszczak, R.G. Bergman, J. Arnold, Chem. Sci. 6 (2015) 993.