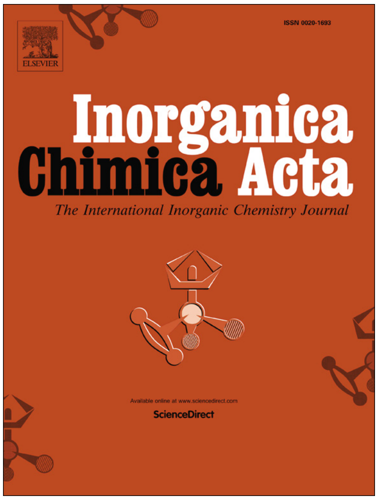

Research paper

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A rare cobalt(III) paramagnetic derivative incorporating 1-alkyl-2-[(o-thioalkyl)phenylazo]imidazole (SMeaaiNEt) : EPR, redox and magnetic interpretation

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ABSTRACT

The condensation of 1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole (SMeaaiNEt), $Co(ClO_4)_2$, $6H_2O$ and NaN_3 in methanol affords a rare Co(III) paramagnetic complex $[Co(SMeaaiNEt)(N_3)_3]$ (**1**). Single crystal X-ray diffraction study of complex **1** reveals that the Co(III) possesses a distorted octahedral environment. The EPR study interprets an unusual high-spin Co(III) species with configuration $t_{2g}^4e_g^2$ and $S = 2$. The temperature dependent magnetic interpretation agrees with the existence of intermolecular antiferromagnetic coupling on the paramagnetic Co(III) center. A Cyclic voltammetry study displays for complex **1** two quasi-reversible and one irreversible responses at the negative direction which may be assigned to different reduction systems. DFT computation using optimized geometry is governed to explain the electronic nature of cobalt derivative which is in accordance with the experimental evidence.

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1. Introduction

There has been a continuous interest in the chemistry of metal complexes of imidazole and related heterocycles [1-4]. There are two basic reasons among the researchers to concentrate on imidazole type systems: biochemical ubiquity and an alternative to polypyridines. The metal complexes of polypyridines have received much attention because of rich electrochemistry, interesting optical properties, bioinorganic chemistry and catalysis [5-10]. This has led to the modification of the ligand system inserting different substituents, presence of other donor centers etc [11-14]. Ligand synthesis using imidazole as heterocyclic backbone is of much advantage because of the biochemical importance of this molecule [15,16]. Imidazole carries meta-related two N centers of different basicity and can bind strongly heavy metal ions [17,18]. We have designed a surface modified extractant by anchoring imidazole to polystyrene by azo group (–N=N–) and have been used for the separation of heavy metals from drinking water, environmental samples, medicinal samples and ores, minerals [19]. The fundamental property of interaction between metal ions and organic ligands has been utilized in the design of functional materials. Azoimidazoles is one such system. It has also been used to extract anions through protonation of imidazole motif and subsequent interaction with anions via hydrogen bonding [20]. The exo-bidentate behavior of the ligand has been eliminated by N(1)-alkylation. The coordination chemistry of 1-alkyl-2-(arylazo)imidazoles (RaaiR′) has been studied by us [21-27] and others [28,29] using transition metals. In RaaiR′, the active function is the azoimine group (–N=N–C=N–) which is isoelectronic with diimine function (–N=C–C=N–). The non-transition metal complexes of arylazoimidazole has been reported earlier [30-33]. The Group 12 metal complexes of RaaiR′ show both monodentate imidazole-N and chelating *N*,*N*′-donor ligands [30-34]. Co(III) complexes may exist in diamagnetic low-spin (t_{2g}^6) and/or paramagnetic high-spin ($t_{2g}^4e_g^2$) octahedral geometry. In most cases $[Co(III)L_6]^{n+}$ octahedral complexes are diamagnetic. Other than CoF_3, $[CoF_3(H_2O)_3]$ and $[CoF_6]^{3-}$ recent literature shows few Co(III) complexes with N, O donor ligands that may exhibit temperature dependent paramagnetism [36-38]. Herein, we report the azido-Co(III) complex incorporating1-alkyl-2-[(*o*thioalkyl)phenylazo]imidazole (SMeaaiNEt) (**1**). Complex **1** is spectroscopically characterized and structurally confirmed by single crystal X-ray diffractometry. Variable temperature magnetic measurement confirms the existence of strong antiferromagnetic coupling on the Co(III) center. The redox and EPR spectrometric studies are also reported.

2. Experimental

2.1. Materials

All chemicals and solvents were of reagent grade and used as received. $Co(ClO_4)_2.6H_2O$, *o*-(amino)thiophenol, methyl iodide (MeI), ethyl iodide (EtI), NaN_3 are purchased from E. Merck, India. All experiments are carried out under N_2 atmosphere. The ligand is prepared by coupling of *o*-(thioalkyl)phenyldiazonium ion (obtained by diazotization of *o*-(thioalkyl)aniline) and imidazole at pH 7 followed by N(1)-alkylation using alkyl iodide in presence of NaH in dry THF under inert conditions [39].

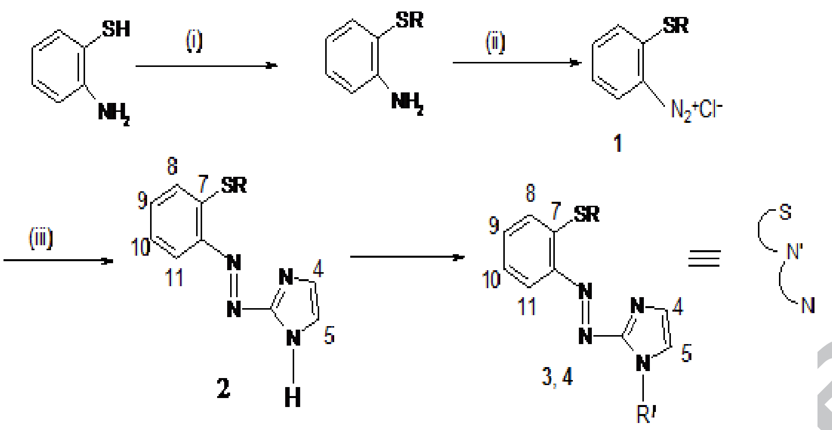
Physical measurements

Microanalytical data (C, H, and N) were collected on a Perkin–Elmer 2400 CHNS/O elemental analyzer. FTIR spectra were recorded on a Perkin-Elmer RX-1 spectrophotometer in the range 4000–400 cm^{-1} as KBr pellets. Electronic spectra were measured on a Lambda 25 (U.V.–Vis.–N.I.R.) spectrophotometer in methanol. EPR spectra were recorded from 0 to 10000 Gauss in the temperature range 77-298 K with an X-band (9.4 GHz) Bruker EMX spectrometer equippedwith an HP 53150A microwave frequency counter. The magnetic properties were investigated with a Quantum Design MPMS-XL superconducting quantum interference device magnetometer (SQUID) at an applied field 0.5 T in a temperature range 5-300 K. Powder samples were measured in a pharmaceutical cellulose capsule.

Electrochemical measurements were performed using computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disk electrodes. All measurements were carried out under nitrogen environment at 298 K with reference to SCE in acetonitrile using [nBu$_4$N][ClO$_4$] as supporting electrolyte. The reported potentials are uncorrected for junction potential.

Synthesis of [Co(SMeaaiNEt)(N$_3$)$_3$] (1)

1-Ethyl-2-[*o*-(thiomethyl)phenylazo]imidazole (SMeaaiNEt) (0.2 g,0.81 mmol) in methanol (15 ml) was added drop wise to Co(ClO$_4$)$_2$.6H$_2$O (0.3 g, 0.82 mmol) in the same solvent (10 ml) at 298 K under N$_2$ environment. To this solution NaN$_3$ (0.10 g, 1.52 mmol) was added in small volume of water. The solution was stirred for 3 hrs. Orange-brown solution was then filtered off and N$_2$ gas was bubbled to reduce its volume to 10 ml. The solution was then kept into refregerator for 12 hrs. Dark brown mass was precipitated at the bottom of the container and filtered. Residue was then washed with methanol-water (1:1, v/v) and shining dark brown crystals were separated out after few days on slow evaporation of the solvent. Then good shaped block crystals were air-dried before X-ray diffraction analysis. Yield was 0.22 g (60%). Anal. Calc. for$C_{12}H_{14}CoN_{13}S$: C, 33.41; H, 3.27; N, 42.19. Found: C, 33.66; H, 3.41; N, 41.87%. The **Scheme 1** depicts the synthesis of the ligand.



Scheme 1. (i) Dry EtOH/Na, RX; (ii) $NaNO_2$/HCl, 0-5°C; (iii) Imidazole, Na_2CO_3 solution (pH ~ 7); (iv) THF/NaH, $R^{/}X$ (R = Me, $R^{/}$ = Et).

X-ray crystallography

The crystal structure of **1** was determined by X-ray diffraction method. Crystal data and experimental details for data collection and structure refinement are reported in **Table 1**. Intensity data and cell parameters were recorded at 298(2) K on a Bruker Breeze (MoKα radiation λ = 0.71073 Å) equipped with a CCD area detector and a graphite monochromator. The ω: 2θ scan technique was applied within a θ range of 1.62–27.47°. No significant crystal decay was observed. The raw frame data were processed using SAINT and SADABS to yield the reflection data file [40,41]. The structure was solved by Direct Methods using the SIR97 program [42] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program [43] in the WinGX suite v.1.80.05 [44]. All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry and refined "riding" on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/\ [\sigma^2 F_o^2 + (0.0520P)^2 + 0.3154P]$, where $P = (F_o^2 + 2F_c^2)/3$. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1499217 for **1** and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2IEZ, UK (fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data of compound **1**.

Empirical formula	$C_{12}H_{14}CoN_{13}S$
Formula weight	431.35
Temperature	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
a, Å	8.3359(10)
b, Å	8.879(2)
c, Å	13.3259(14)
α, deg	77.966(16)

β, deg	72.018(9)
γ, deg	69.633(14)
Volume, Å^3	873.8(2)
Z	2
D_{calc} (mg m^{-3})	1.639
μ(Mo Kα) (mm^{-1})	1.118
Crystal size	0.46$\times$0.40 $\times$0.32
F(000)	440
θ range for data collection	1.62–27.47
Reflections collected / unique	4013 / 3445 [$R(int)$ = 0.0175]
Data / restraints / parameters	3445 / 0 / 246
Final R indices [$F_o>4\sigma(F_o)$]^b	$R1$ = 0.0299, $wR2$ = 0.0776
R indices (all data)	$R1$ = 0.0403, $wR2$ = 0.1002
Largest diff. Peak and hole, $e.Å^{-3}$	0.381 and -0.311

[a] Goodness-of-fit S = [$\Sigma w(F_o^2-F_c^2)^2$/ (n-p)]1/2, where n is the number of reflections and p the number of parameters. [b] $R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Results and discussion

Synthesis and formulation

$Co(ClO_4)_2.6H_2O$ reacts with 1-alkyl-2-[*o*-(thiomethyl)phenylazo]imidazole (SMeaaiNEt) and NaN_3 (1:1:2 moleproportion) in methanol to generate $[Co(SMeaaiNEt)(N_3)_3]$ (**1**) which is isolated as dark brown crystals on slow cooling (**Scheme 2**). The composition of the complex is supported by micro-analytical data. Complex **1** is soluble in methanol, ethanol, chloroform, dichloromethane and acetonitrile but insoluble in hexane, benzene, and toluene. The IR spectra of **1** is determined on comparing with the free ligand and some reported cobalt(II) complexes of arylazoimidazoles [45,46]. The characteristic strong transmission band at 2050-2115 cm^{-1} is referred to νN_3 that suggests the terminal azide bonding undoubtedly [47]. Moderately intense stretching bands at 1570-1600 and 1420–1452 cm^{-1} are observed due to $\nu(C=N)$ and $\nu(N=N)$, respectively, for the coordinated SMeaaiNEt ligand.

$$Co(ClO_4)_2.6H_2O + SMeaaiNEt + 3NaN_3 \longrightarrow [Co(SMeaaiNEt)(N_3)_3]$$

Scheme 2. Reaction scheme for the synthesis of complex **1**.

Molecular structure

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group $P\overline{1}$. Selected bond distances and bond angles are given in **Table 2**. The asymmetric unit consists of three azide anions and ligand SMeaaiNEt coordinated to a cobalt center, featuring a mononuclear complex. The reaction is started taking $Co(ClO_4)_2$ as metal salt; however, at the end a Co(III) metal complex is formed; so, air O_2 might be the oxidizing agent during synthesis. Two nitrogen atoms (N2 and N4) and one sulfur atom (S1) belonging to ligand L coordinate with the metal center in a chelating manner, while the other three positions are occupied by three nitrogen atoms (N5, N8 and N11) from three different azide ions (see **Figure 1**). As shown in **Figure 1**, the Co1(II) center adopts a six-coordinated $\{CoN_5S\}$ distorted octahedral geometry.

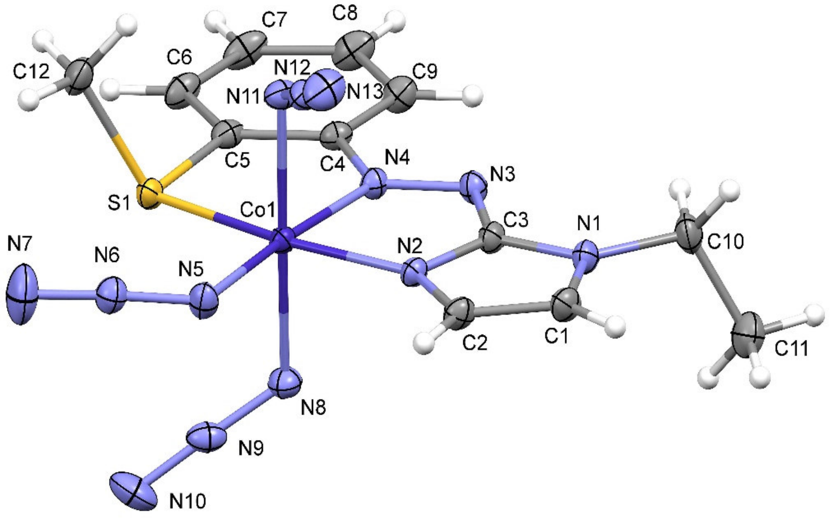


Figure 1. The ORTEP view of complex **1**. The ellipsoids are drawn with 30% probability level.

The Co1-N distances in **1** lie in the range of 1.899(19)-1.970(2) Å which are comparable with reported distances of Co(III)-N(sp^2) length (1.89-2.02 Å) [48-50]. The paramagnetic Co(III) complexes show longer bond length because of electron population in e$_g$ level [51]. The Co(II)-N(sp^2) distances lie in the range of 2.02-2.15 Å which is longer than Co(III) complexes; either in diamagnetic or paramagnetic nature. The Co(II)-N(azo) distance in the family of 1-alkyl-2-(arylazo)imidazole complexes belongs in the range of 2.33-2.52 Å [52-55]. The bond parameters in the present complex well fit to Co(III) oxidation state. The Co1-S distance 2.239(7) Å is also comparable with earlier literature of thioether-salicylaldimines [50]. A supramolecular network is formed through the cooperation between the monomeric units. Only two C-H···N hydrogen bonds are detected of distances C(6)-H(6)…N(7) = 2.51 and C(12)-H(12A)…N(11) = 2.45 Å and π···π interactions of about 3.704 Å between the monomeric units helps in stabilizing the framework (**Figures 2a** and **2b**).

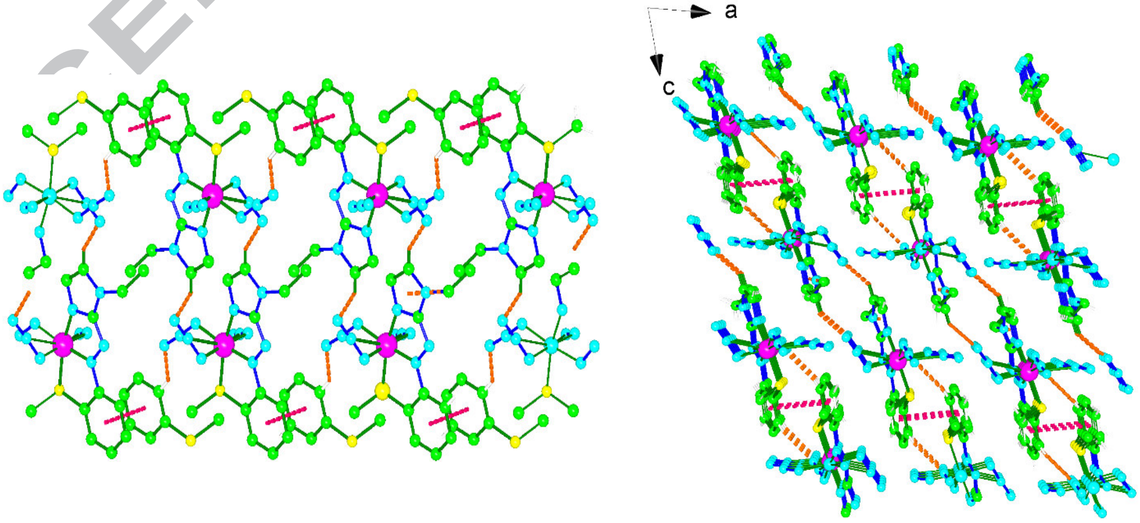


Figure 2. (a) Weak interactions like C–H···N hydrogen bonding (orange) and π···π interactions (dark pink) can be observed between the monomeric units; (b) view of the framework along the *b* axis.

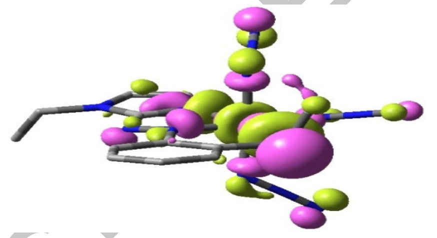
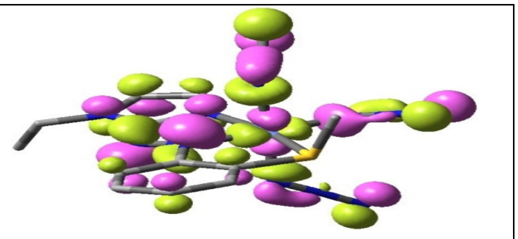
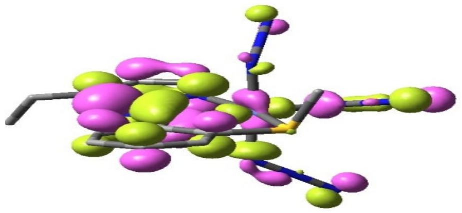
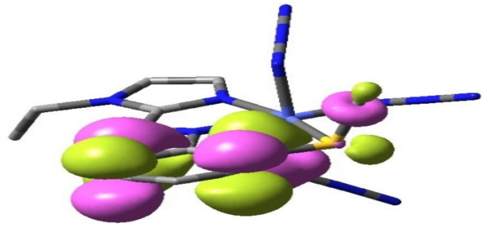
Table 2. Selected bond distances and bond angles of complex **1**.

Co(1)- N(4)	1.8989(19)	N(4)- Co(1)- N(2)	80.54(8)
Co(1)- N(2)	1.9142(18)	N(4)- Co(1)- N(5)	173.58(8)
Co(1)- N(5)	1.915(2)	N(2)- Co(1)- N(5)	93.06(9)
Co(1)- N(11)	1.957(2)	N(4)- Co(1)- N(11)	88.55(9)
Co(1)- N(8)	1.970(2)	N(2)- Co(1)- N(11)	90.11(9)
Co(1)- S(1)	2.2387(7)	N(5)- Co(1)- N(11)	91.10(10)
		N(4)- Co(1)- N(8)	88.62(9)
N(4)-Co(1)-S(1)	87.28(6)	N(2)- Co(1)- N(8)	90.74(9)
N(2)- Co(1)- S(1)	167.65(6)	N(5)- Co(1)- N(8)	91.86(10)
N(5)- Co(1)- S(1)	99.13(7)	N(11)- Co(1)- N(8)	176.87(9)
N(11)-Co(1)-S(1)	91.65(7)	N(8)-Co(1)-S(1)	86.89(7)

Electronic spectra

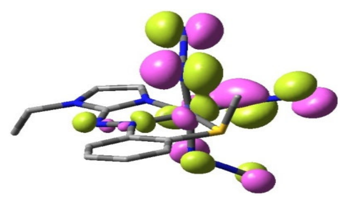
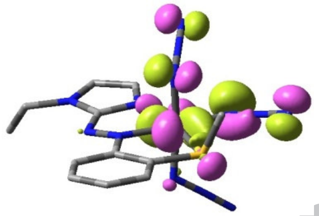
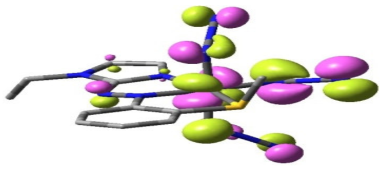
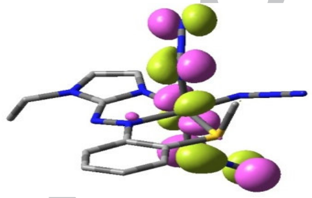
The electronic spectra of the ligand and complex **1** were recorded in HPLC grade acetonitrile solution. Visible region of the complex spectrum shows three transitions: the transitions are 600-675, 450-515, 385-425 nm along with two transitions in UV region; 355-375, 240-255 nm. Based on the low intensity and low energy nature the bands are considered to be d–d transitions in an octahedral geometry. The high intense transition <430 nm may be assigned to MLCT transitions.

Theoretically generated structures of complex **1** are used to calculate composition and energy of the functions to explain the electronic properties. The orbital energies alongwith contributions from the ligands and metal are given in ESI (**Tables S1** and **S2**). **Figure 3** depicts the selected occupied and unoccupied frontier orbitals. The HOMO of **1** is constituted by Co (22%), ligand, SMeaaiNEt (40%), and N_3^- (38%). The other occupied MOs (HOMO-2, HOMO-3 etc) are mainly contributed from N_3^- (>80%). Unoccupied MOs are contributed from SMeaaiNEt (>95%). The calculated transitions are grouped in **Table S2**. The intensity of these transitions is assessed from oscillator strength (*f*). Here the visible region (400-570 nm) transitions are assigned to HOMO-6→LUMO+3, HOMO-8→LUMO etc. The calculated transitions at 470-570 nm are weak (*f*, 0.0118–0.0934) and are assigned to a mixture of LMCT (ligand-to-metal charge transfer) and ILCT (intra-ligand charge transfer). An intense band is observed at 450 nm which is ILCT band.

	
HOMO-1; E, -5.22 eV; N_3, 19%; Co, 35%; NNS, 46%	HOMO; E, -4.7 eV; N_3, 38%; Co, 22%; NNS, 40%
	

LUMO; E, -4.44 eV; N_3, 17%; Co, 14%; NNS, 69%	LUMO+1; E, -2.44 eV; N_3, 01%; Co, 00%;NNS , 99%

(a)

	
HOMO-1; E, -5.95 eV; N_3, 81%; Co, 13%; NNS, 06%	HOMO; E, -5.69 eV; N_3, 31%; Co, 61%; NNS, 08%
	
LUMO; E, -5.27 eV; N_3, 46%; Co, 48%; NNS, 06%	LUMO+1; E, -5.2 eV; N_3, 47%; Co, 49%; NNS, 04%

(b)

Figure 3. Contour plots of some selected (a) α- and (b) β- molecular orbitals of **1**.

EPR spectra

EPR spectra of the polycrystalline complex **1** are recorded in the temperature range 77-298 K. The spectra at 77, 140 and 298 K are reported in **Figure 4**. Almost all of the octahedral Co(III) complexes have diamagnetic ground state and only few exceptions, such as $[CoF_3(H_2O)_3]$ and $[CoF_6]^{3-}$, are known [48]. Therefore, the electronic configuration is t_{2g}^6 and the spin state is $S = 0$; for this state no EPR signal is expected. In contrast, **Figure 4** shows that in the range examined a strong EPR spectrum can be revealed; absorptions of the microwave radiations are observed from

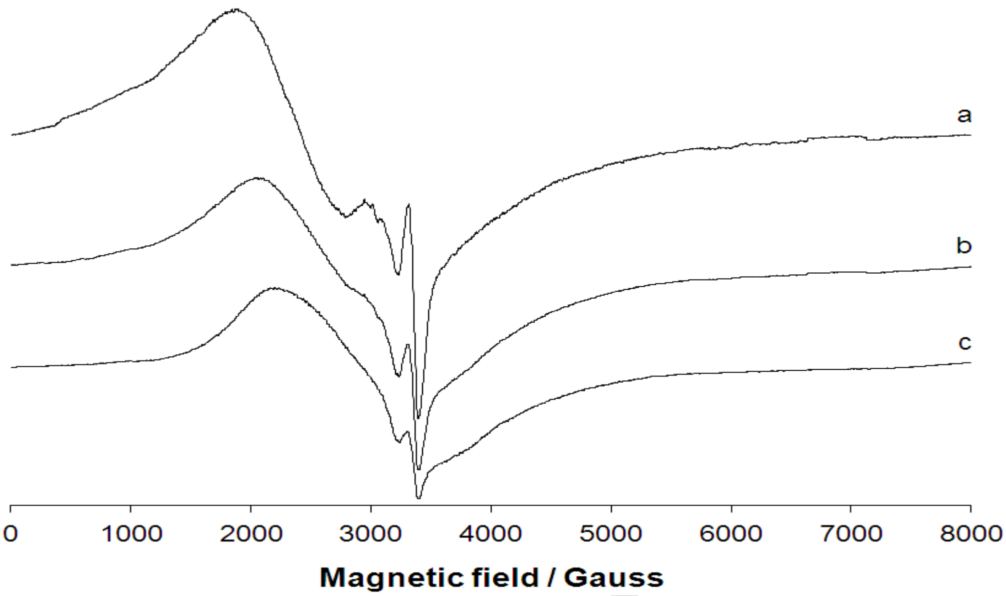


Figure 4. X-band EPR spectra of the polycrystalline complex **1** at: (a) 298, (b) 140 and (c) 77 K. The spectra are recorded with the same instrumental gain.

0 to 5000 G and resonances at *g* 3.6, 2.3 and 2.0 (at 77 K) and at 3.6 and 2.0 plus a shoulder at 1.8 (298 K) are well evident. The spectral pattern does not change significantly with the temperature, but from 77 to 298 K a significant weakening of the signal intensity is detected (cfr. traces a and c of **Figure 4**). The results can be interpreted on the basis of an unusual high-spin Co(III) species with configuration $t_{2g}^4e_g^2$ and S = 2. EPR spectra of other systems with S = 2, such as high-spin Fe(II) and high-spin Mn(III) complexes, support our experimental results [49,50]. It has been pointed out that the chance to detect EPR signals for non-Kramer doublets

increases for $S \geq 2$ and, in particular, the transition within the highest non-Kramer doubletis always by far the easiest to be detected and is often the only observe transition; however, in most of the cases the spectra provide insufficient information for the determination of the Hamiltonian parameters (and this is the case) [50]. The decrease of the EPR signal intensity from 77 to 298 K gain (the three spectra in **Figure 4** are reported using the same instrumental gain) is in agreement with the VTM measurements, which indicate the population of the $S = 0$ state with increasing the temperature.

Complex **1** was dissolved in two types of solvent: a weakly coordinating solvent such as CH_3CN and a coordinating solvent such as DMF. EPR spectra (shown in **Figure 5**) are very different with respect to those recorded in the solid state. In both the cases no signal is revealed (the gain is the same used for the solid samples), and this means that in solution the electronic configuration t_{2g}^6 and the spin $S = 0$ are

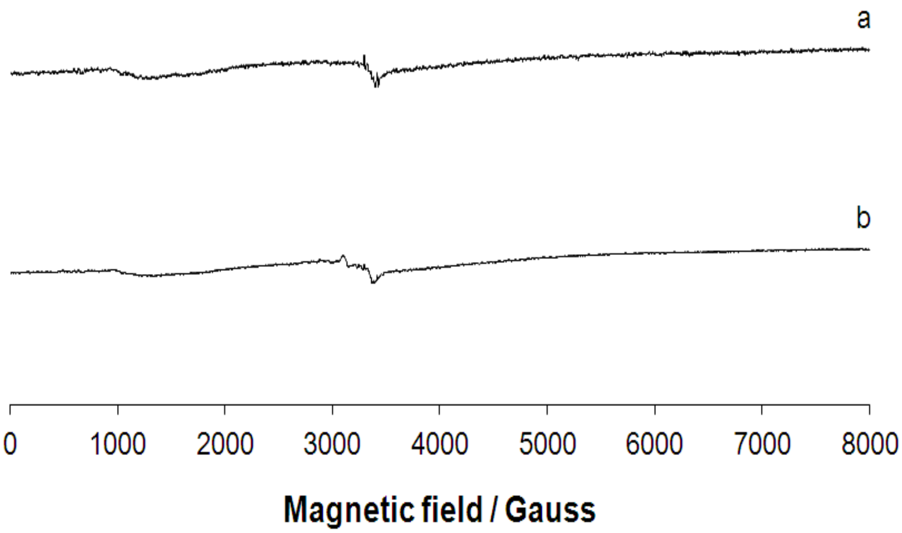


Figure 5. Anisotropic X-band EPR spectra of the complex **1** dissolved in: (a) DMF and (b) CH_3CN. The spectra are recorded with the same instrumental gain used in Figure 4.

favored. Therefore, it is probable that solid stat effects stabilize the anomalous high-spin state, whereas in solution the behavior is that usual for Co(III) complexes.

Magnetic property

The magnetic property of complex **1** in the form of $\chi_M T$ *vs T* plot (χ_M is the molar magnetic susceptibility) is shown in **Figure 6**. The value of $\chi_M T$ at 300 K is 2.39 emu mol^{-1} K which defines high spin Co(III), a typical value for cobalt (III) ion, as expected. In general, Co(III) exists as diamagnetic (low-spin), t_{2g}^6 and paramagnetic (high-spin), $t_{2g}^4 e_g^2$ electronic configuration. However, Co(III) paramagnetic complexes are fewer [59] than those of huge number of diamagnetic Co(III) complexes. The present example is one of the rare case of 1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole Co(III) high-spin paramagnetic complex. With lowering of temperature there is an increasing of $\chi_M T$ to 7.25 emu mol^{-1} K at 12 K and then a rapid decrease to 4.15 emu mol^{-1} K at 5 K. This feature is quite interesting and

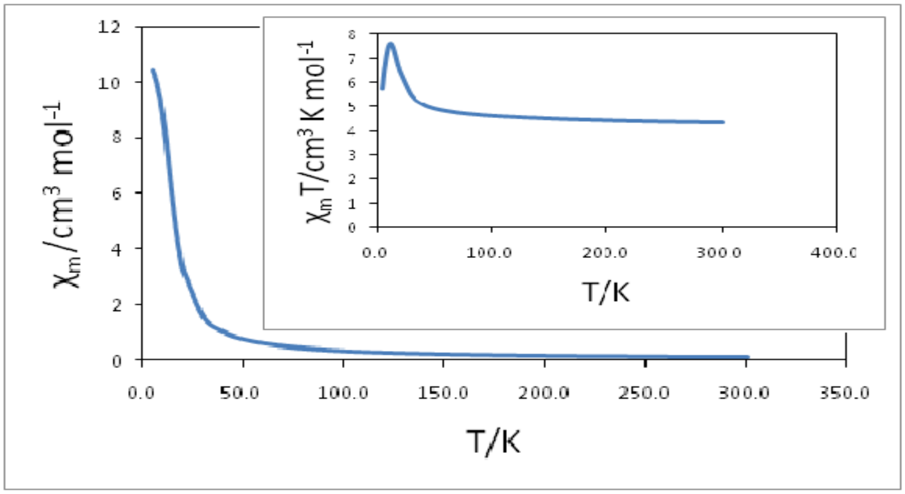


Figure 6. Temperature dependence of χ_M vs T of **1**. Inset shows $\chi_M T$ vs T plot.

stipulates noticeable intermolecular antiferromagnetic interaction. We could come into conclusion that the concerned data clearly supports the mononuclear high-spin Co(III) complex in octahedral symmetry (d^6; HS, S=2).[24] **Figure 6** is evident with the calculated magnetic moment 4.37 BM at 300 K (theoretical value 4.89 BM [51].

Redox study

Cyclic voltammetry is governed to examine the redox nature of the complex in acetonitrile solution having the potential range –1.6 to 1.2 V *vs* SCE electrode. A representative voltammogram is shown in **Figure 7**. The complex displays no characteristic response at the positive part in the redox diagram. On scanning to negative direction (0.0 to -1.6 V) three redox responses are observed at ~ -0.4; -0.8

and -1.4 V. Two of the reductive couples (~ -0.4; -0.8 V) are quasi-reversible ($\Delta Ep \geq$ 100 mV) while third one remains at -1.4 V as irreversible. The couples at negative to SCE are reductive in nature and first two reductions are referred to azo/azo$^-$ and azo$^-$/azo$^=$ respectively [52]. The irreversible reduction at very high negative potential (-1.4 V) may be considered electron accommodation to azido dominated redox level. Cyclic voltammetric behaviour of the complexes is readily accountable from DFT calculation. Unoccupied MOs are significantly dominated by azoimine function, thus reduction may refer to electron accommodation at azo dominated orbital of the ligand. So the assignment, azo reductions are justified. The LUMO and other unoccupied MOs are

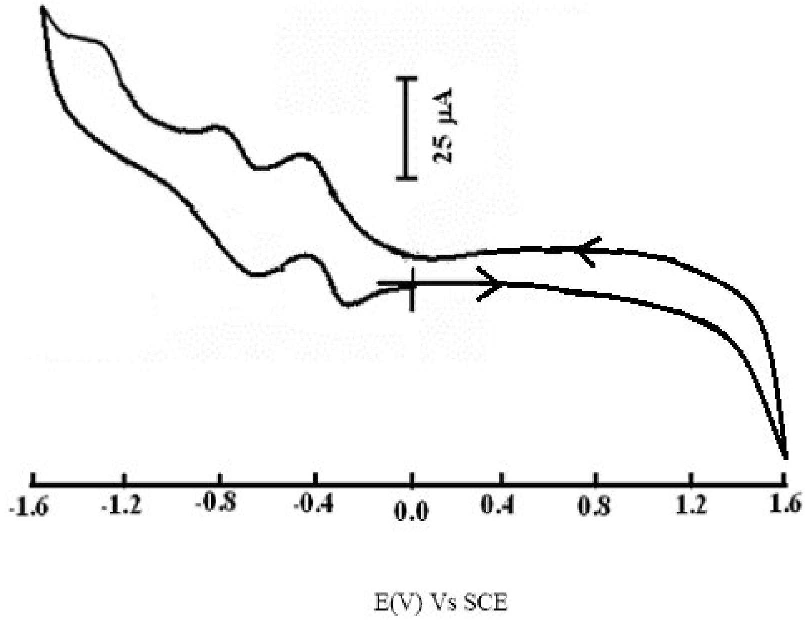
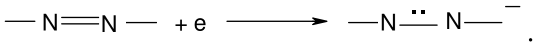


Figure 7. Cyclic voltammogram of complex **1** in MeCN solution (0.1 NBu$^t_4$ClO$_4$) using Pt-milli working electrode, Pt-wire auxiliary and Ag/AgCl reference electrode under nitrogen at 25 °C). SMeaaiNEt dominated (>95%), so reduction is as usual,



Conclusion

Azido-cobalt(III)-1-alkyl-2-[(*o*thioalkyl)phenylazo]imidazole (SMeaaiNEt) complex is afforded and systematically characterized by X-ray crystallography and several spectroscopic techniques. Temperature and solvent dependent EPR spectra are recorded confirming an unusual high-spin Co(III) derivative and well comparable with other high-spin Fe(II) and Mn(III) complexes. Temperature dependent magnetic study reveals the presence of strong antiferromagnetic coupling on the paramagnetic Co(III) center. This phenomenon is very uncommon and probably the first example of the Co(III) derivative coupled with imidazole moiety and monodentate orientation of three azide molecules. Further investigations on DNA cleavage and fluorescence cell-imaging using substituted imidazole assisted cobalt derivatives are currently being carried out in our laboratories.

Acknowledgements

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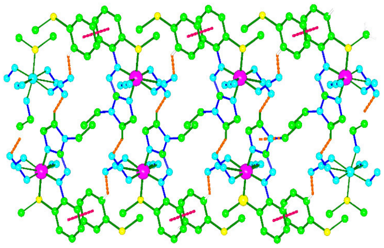
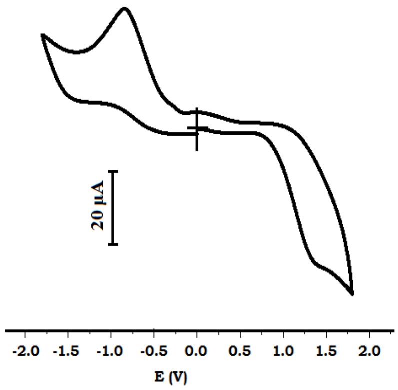
GRAPHICAL ABSTRACT

A rare cobalt(III) paramagnetic derivative incorporating 1-alkyl-2-[(o-thioalkyl)phenylazo]imidazole (SMeaaiNEt) : EPR, redox and magnetic interpretation

Soumendranath Nandi[a], Kuheli Das[a], Amitabha Datta[*,b], Suman Roy[a], Eugenio Garribba[c], Takashiro Akitsu[d], Chittaranjan Sinha[*,a]

1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole (SMeaaiNEt), employed a Co(III) derivative is afforded. The spectroscopic properties are carried out and DFT optimized geometry is also included to explain the electronic nature. EPR spectra strongly supports the unusual high-spin Co(III) species.	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RESEARCH HIGHLIGHTS

A rare cobalt(III) paramagnetic derivative incorporating 1-alkyl-2-[(o-thioalkyl)phenylazo]imidazole (SMeaaiNEt) : EPR, redox and magnetic interpretation

Soumendranath Nandi[a], Kuheli Das[a], Amitabha Datta[*,b], Suman Roy[a], Eugenio Garribba[c], Takashiro Akitsu[d], Chittaranjan Sinha[*,a]

√ 1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole Co(III) complex

√ Structural confirmation by single crystal X-ray diffraction

√ Variable temperature magnetism and intermolecular antiferromagnetic coupling

√ Cyclic voltammetry shows two quasi-reversible and one irreversible responses

√ EPR spectra an unusual high-spin Co(III) species with configuration $t_{2g}^4e_g^2$