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Oxovanadium(V) and Cobalt(III) Complexes of Dithiocarbazate-Based Schiff Base Ligands: Formation of a Thiadiazole Ring by Vanadium-Induced Cyclization of the Coordinated Ligand

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S-Methyl 3-((2-hydroxyphenyl)methyl)dithiocarbazate (H_2L^1) and its bromo derivative (H_2L^2), which are traditionally biprotic tridentate (ONS) ligands, behave in an unprecedented manner when allowed to react with $[VO(acac)_2]$ under an oxidative environment in acetonitrile–water medium containing a catalytic amount of alkali metal ion. The products obtained are oxovanadium(V) compounds $[VOL(L_{cyclic})]$ ($L = L^1$, **1a**, and L^2, **1b**) that contain one molecule of ligand which undergoes metal-induced cyclization to form a thiadiazole ring. Compound **1a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.1830(9)$ Å, $b = 9.4165(12)$ Å, $c = 12.700(2)$ Å, $\alpha = 100.988(8)^o$, $\beta = 100.195(7)^o$, $\gamma = 78.774(8)^o$, $V = 1046.3(2)$ Å^3, and $Z = 2$. With cobalt(III), however, the products $[CoL(HL)]{\cdot}H_2O$ ($L = L^1$, **2a**, and L^2, **2b**) have hydrogen-bonded dimeric structures with each ligand virtually carrying 1.5 units of negative charge as confirmed by X-ray crystal structure analysis of **2a**. It also crystallizes in triclinic space group $P\bar{1}$ with $a = 12.0842(8)$ Å, $b = 13.5251(9)$ Å, $c = 14.1960(10)$ Å, $\alpha = 78.122(6)^o$, $\beta = 73.888(6)^o$, $\gamma = 78.255(6)^o$, $V = 2154.7(3)$ Å^3, and $Z = 4$. In solution, **2a** is a symmetric molecule as indicated by ^{1}H NMR, involving a characteristic hydrogen-bonded O–H–O broad feature in the downfield (at 14.5 ppm) connecting both monoprotonated (LH^-) and deprotonated (L^{2-}) forms of the ligand—a situation somewhat analogous to the classic H–F–H case as observed in bifluoride ion.

Introduction

In earlier reports we[1−4] as well as others[5−12] have shown that *S*-methyl 3-((2-hydroxyphenyl)methyl)dithiocarbazate (H_2L^1) and related molecules can act as biprotic tridentate ONS donor ligands during their complexation with transition metal ions. Coordination chemistry of oxometalate ions with tridentate ligands (L) has an intrinsic advantage because of the latter's ability to form an MOL primary core with at least one or more available metal coordination site(s) for the acceptance of ancillary ligands.[13,14] We have tried to harness this coordination possibility for the generation of structurally and kinetically interesting mono-, bi-, and polynuclear oxometalate complexes using H_2L^1 and related molecules as tridentate ligands.[1−4]

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Recently we have been successful in isolating neutral complexes of overall compositions $V^{V}O(L)_2$ and $Co^{III}(L)_2$ ($L = L^1$ and L^2) by allowing H_2L^1 and its bromo derivative (H_2L^2) to react with $[VO(acac)_2]$ and $Co(CH_3COO)_2 \cdot 4H_2O$, respectively, under an oxidative environment. The intriguing feature of these reactions is the compensation of three units of cationic charge by two molecules of these ligands, giving indications that the complexation behavior of these traditionally tridentate biprotic ligands is not straightforward and demands further investigation. Herein, we report the synthesis, crystal and molecular structures, spectroscopic characterization, and redox properties of mononuclear oxovanadium(V) and cobalt(III) complexes of the aforesaid ONS ligands, showing the diversities in their coordination properties.

Experimental Section

The tridentate ligands (H_2L^1 and H_2L^2)[15] and the precursor complex $[VO(acac)_2]$[16] (Hacac = acetylacetone) were prepared by following reported methods. Reagent grade solvents were dried from appropriate reagents[17] and distilled under nitrogen prior to their use. All other chemicals were commercially available and used as received.

Preparation of Complexes. $[VOL^1(L^1_{cyclic})]$ (1a). To a stirred solution of $[VO(acac)_2]$ (0.4 g, 1.5 mmol) in acetonitrile (30 mL) was added 0.68 g (3.0 mmol) of the ligand (H_2L^1) as a solid. The resulting mixture was heated at reflux for 10 min, when a clear brown solution was obtained. To this was then added an aqueous solution (ca. 10 mL) of cesium nitrate (0.03 g), and the mixture was refluxed further for ca. 3 h. A green solution obtained at this stage was allowed to stand overnight in the air. The product was collected by filtration, washed with methanol, and dried in vacuo. Diffraction-quality crystals were picked up from this batch for X-ray structure analysis. Yield: 0.25 g (32%). Anal. Calcd for $VC_{18}H_{15}N_4O_3S_4$: C, 42.02; H, 2.92; N, 10.89. Found: C, 41.80; H, 2.95; N, 10.68. IR (KBr disk) (cm^{-1}): $\nu(C\overset{\cdots}{-}N)$, 1600 s; $\nu(C\overset{\cdots}{-}O$/phenolate), 1545 s; $\nu(V{=}O_t)$, 960 s; $\nu(C{-}S)$, 650 m. ^1H NMR (300 MHz, CD_2Cl_2, 23 °C) [δ/ppm, multiplicity, integration (assignment)]: 8.87, s, 1H (azomethyne); 7.80−6.78, m, 8H (aromatic); 2.49 and 2.40, a pair of singlets, 6H (SCH_3 groups).

One can also use lithium acetate dihydrate instead of cesium nitrate to carry out the above reaction successfully.

$[VOL^2(L^2_{cyclic})]$ (1b). This compound was obtained as dark brown crystals in 25% yield by following the method as described above for **1a**, except that H_2L^2 was used as the tridentate ligand instead of H_2L^1. Anal. Calcd for $VC_{18}H_{13}N_4O_3S_4Br_2$: C, 32.14; H, 1.93; N, 8.33. Found: C, 32.03; H, 2.05; N, 8.48. IR (KBr disk) (cm^{-1}): $\nu(C\overset{\cdots}{-}N)$, 1610 s; $\nu(C\overset{\cdots}{-}O$/phenolate), 1550 s; $\nu(V{=}O_t)$, 960 s; $\nu(C{-}S)$, 650 m.

$[Co^{III}L^1(HL^1)]\cdot H_2O$ (2a). To a freshly prepared solution of H_2L^1 (0.23 g, 1 mmol) in hot ethyl alcohol (20 mL) was added with stirring a stoichiometric (2:1 mol ratio) amount of cobalt(II) acetate tetrahydrate (0.13 g, 0.5 mmol), also in ethyl alcohol (10 mL). The resulting brown solution was refluxed for 30 min, filtered, rotary evaporated to ca. 15 mL volume, and left in the air for an overnight period to yield a dark brown shining crystalline product, which was washed with methanol−ether (1:2 v/v) and dried in vacuo. The product was again dissolved in dichloromethane and layered with hexane to obtain brown crystals suitable for single-crystal X-ray analysis. Yield: 0.13 g (49%). Anal. Calcd for $CoC_{18}H_{19}N_4O_3S_4$: C, 41.07; H, 3.61; N, 10.65. Found: C, 41.18; H, 3.80; N, 10.54. IR (KBr disk) (cm^{-1}): $\nu(C\overset{\cdots}{-}N)$, 1595 s; $\nu(C\overset{\cdots}{-}O$/phenolate), 1470 s; $\nu(C{-}S)$, 650 m. ^1H NMR (300 MHz, CD_2Cl_2, 23 °C) [δ/ppm, multiplicity, integration (assignment)]: 14.5 b s, 1H ($O{-}H\cdots O$); 7.45, m, 4H (aromatic ring); 7.05, m, 6H (four aromatic ring protons + two azomethyne protons); 2.54, s, 6H (SCH_3).

Table 1. Crystal Data and Structure Refinement for **1a** and **2a**

param	1a	1b
formula	$C_{18}H_{15}N_4O_3S_4V$	$C_{18}H_{19}CoN_4O_3S_4$
fw	514.52	526.54
T, K	293(2)	293(2)
cryst system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	4
a, Å	9.1830(9)	12.0842(8)
b, Å	9.4165(12)	13.5251(9)
c, Å	12.700(2)	14.1960(10)
α, deg	100.988(8)	78.122(6)
β, deg	100.195(7)	73.888(6)
γ, deg	78.774(8)	78.255(6)
V, Å^3	1046.3(2)	2154.7(3)
d_{calc}, Mg/m^3	1.633	1.623
θ range, deg	2.29−27.50	2.34−27.50
F(000)	524	1080
cryst size, mm	0.14 × 0.49 × 0.38	0.38 × 0.88 × 0.45
radiation used	Mo Kα	Mo Kα
μ, mm^{-1}	0.902	1.213
no. reflcns collcd	5092	10 303
no. indpdt reflcns	4794 (R_{int} = 0.0148)	9839 (R_{int} = 0.0247)
no. of params	288	599
R1 (wR2) [$I > 2\sigma(I)$]	0.0351 (0.0894)	0.0369 (0.0868)
R1 (wR2) (all data)	0.0449 (0.0952)	0.0537 (0.0951)
GOF (F^2) (all data)	1.043	1.019

$[Co^{III}L^2(HL^2)]\cdot H_2O$ (2b). This compound was obtained in 32% yield as dark brown crystals by following the same procedure described for **2a**, except that H_2L^2 was used as the ligand. Anal. Calcd for $CoC_{18}H_{17}N_4O_3S_4Br_2$: C, 31.58; H, 2.48; N, 8.19. Found: C, 31.67; H, 2.42; N, 8.11. IR (KBr disk) (cm^{-1}): $\nu(C\overset{\cdots}{-}N)$, 1595 s; $\nu(C\overset{\cdots}{-}O$/phenolate), 1465 s; $\nu(C{-}S)$, 695 m.

Physical Measurements. Details of elemental (C, H, and N) analyses and IR and UV−vis spectral measurements were described elsewhere.[2,18] The ^1H NMR spectra were recorded on a Bruker model Avance DPX-300 spectrometer. Electrochemical measurements were carried out at ambient temperature on a PAR 362 scanning potentiostat using mixed solvent (dichloromethane−acetonitrile, 3:1 v/v) solutions containing 0.1 M Et_4NClO_4 (TEAP) as background electrolyte. A platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode were used. Bulk electrolysis was performed with the use of a Pt-gauze working electrode. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as the internal standard.[19]

X-ray Crystallography. Selected crystallographic data are given in Table 1, and complete data are given in the CIF file. Data were

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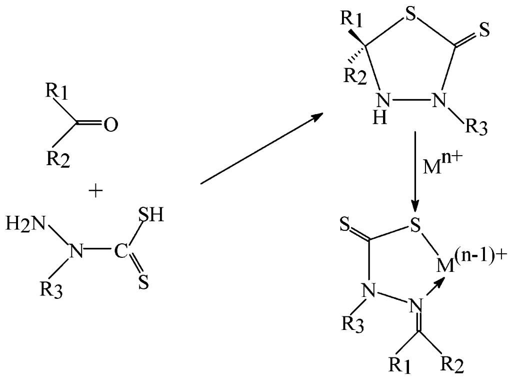
Scheme 1



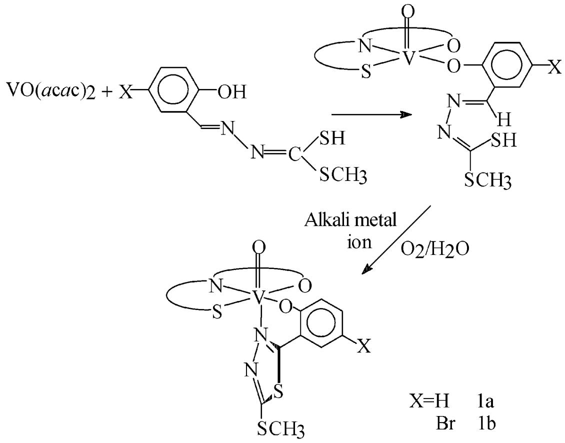
collected at room temperature on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo Kα X-radiation ($\lambda = 0.710\,73$ Å) and the $\theta-2\theta$ technique over a 2θ range of 3−55°. During data collection three standard reflections were measured after every 97 reflections. The structure was solved by direct methods and Fourier difference maps using the SHELXTL-PLUS[20] package of software programs. Final refinements were done using SHELXL-93[21] minimizing $R2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. All non-hydrogen atoms were refined as anisotropic, and the hydrogen atomic positions were fixed relative to the bonded carbons with the isotropic thermal parameters fixed.

Results and Discussion

Synthesis. Schiff base condensation of dithiocarbazic acids generates thiadiazoline-2-thione derivatives by an internal ring closure reaction.[22] These heterocyclic products, on being treated with metal ions, undergo ring opening to produce the metal complexes of the corresponding Schiff base ligand[23] (Scheme 1). The observed chemistry is very much similar to those of thiazoline derivatives formed by the Schiff base condensation of aminothiols.[24]

With this chemistry in mind, the work described here is quite unusual and interesting. Compunds **1a,b** are obtained by refluxing [VO(acac)$_2$] with the tridentate ligands (H_2L^1 and H_2L^2), using a 1:2 metal-to-ligand ratio in acetonitrile−water medium containing a catalytic amount of alkali metal ion. The obligatory steps in this preparative procedure are the presence of water and alkali metal ions in the reaction medium and its subsequent exposure to atmospheric oxygen, as confirmed by several control experiments which include attempted preparations in the absence of alkali metal ions. The products (**1a,b**) obtained have two molecules of ligand. One is coordinated in the usual manner as a tridentate (ONS) biprotic ligand,[1−4] leaving a maximum of two metal coordination sites (considering an octahedral geometry) available for the second incoming ligand. This compulsion probably forces the second ligand (with a likely initial attachment to the metal center through the phenoxo end) to bend in the reverse direction to generate, under an oxidative environment, a thiadiazole ring that remains coordinated to the metal center through a ring nitrogen atom (Scheme 2), thus providing an energetically favored more compact molecular structure. The role of alkali metal ion here is not precisely known at this time.

Scheme 2



In the case of cobalt(III) complexes (**2a,b**), 1:2 metal-to-ligand ratio and exposure to atmospheric oxygen are also required to obtain neutral complexes of 1:2 metal−ligand stoichiometry as observed in the vanadium complexes (**1a,b**). X-ray crystal structure analysis of **2a** has confirmed these molecules to have a composition $[\mathrm{Co^{III}L(HL)}]\cdot H_2O$ with a hydrogen-bonded dimeric structure (vide infra). Thus, of the two ligand molecules (H_2L) here, one is coordinated in the usual manner[1−4] in the tridentate doubly deprotonated form while the second one is monoprotonated, retaining the phenolic OH proton and coordinated as tridentate ligand to generate a neutral octahedral cobalt(III) complex.

IR spectra of the complexes contain all the pertinent bands of the coordinated tridentate ligands.[1−4] In addition, **1a,b** display a strong band at 960 $\mathrm{cm^{-1}}$ due to terminal $\nu(\mathrm{V{=}O_t})$ stretch. One interesting feature is the appearance of a phenoxo stretch (ν(C$\overset{\cdots}{-}$O/phenolate)) at 1550 $\mathrm{cm^{-1}}$ in the vanadium complexes (**1a,b**). The corresponding band in **2a,b** shows a significant shift to lower wavenumber at 1470 $\mathrm{cm^{-1}}$, indicating a bridging mode of attachment of the phenoxo group in the cobalt(III) complexes with the involvement of strong hydrogen bonding.

Description of Crystal Structures. [VL^1(L$^1_{\mathrm{cyclic}}$)]. The crystal structure determination of **1a** confirms the presence of a thiadiazole ring in this molecule formed by intramolecular cyclization of one of the coordinated ligands. An ORTEP view of this molecule is shown in Figure 1, and the selected interatomic parameters are listed in Table 2. It comprises of one tridentate and a bidentate cyclized ligand (referred to as L_{cyclic}), coordinated to a $\mathrm{VO^{3+}}$ unit. The V atom in the molecule is six coordinated, existing in a distorted octahedral geometry in which the axial positions are taken up by the terminal oxygen atom and the N(1B) atom from the L_{cyclic} ligand, the O−V−N(1B) angle being 178.13(9)°. The square plane about the V atom is not strictly planar with

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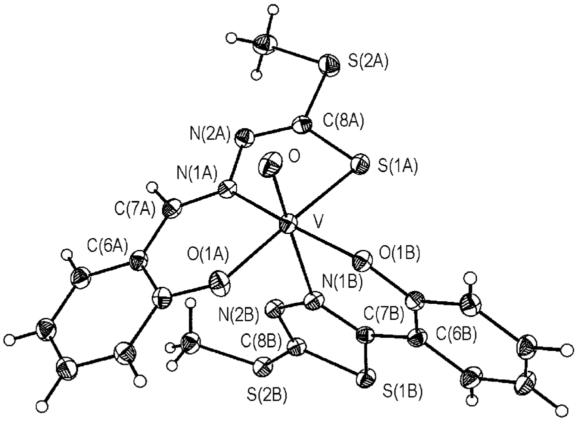

Figure 1. Molecular structure of [VOL^1(L$^1_{cyclic}$)] (**1a**), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Distances and Angles for [VOL^1(L$^1_{cyclic}$)] (**1a**)

Distances (Å)			
V−O	1.598(2)	V−S(1A)	2.3883(7)
V−O(1A)	1.874(2)	V−O(1B)	1.823(1)
V−N(1A)	2.114(2)	V−N(1B)	2.342(2)
C(7A)−S(1A)		C(7B)−S(1B)	1.738(2)
C(6A)−C(7A)	1.425(3)	C(6B)−C(7B)	1.454(3)
C(7A)−N(1A)	1.291(3)	C(7B)−N(1B)	1.309(3)
N(2A)−C(8A)	1.287(3)	N(2B)−C(8B)	1.300(3)
N(1A)−N(2A)	1.413(3)	N(1B)−N(2B)	1.380(2)
C(8A)−S(1A)	1.733(2)	C(8B)−S(1B)	1.732(2)
Angles (deg)			
O−V−O(1A)	100.90(9)	O−V−O(1B)	100.51(8)
O−V−N(1A)	94.07(8)	O−V−N(1B)	178.13(9)
O−V−S(1A)	96.47(7)	O(1B)−V−N(1A)	161.24(7)
O(1B)−V−N(1B)	79.96(7)	O(1B)−V−O(1A)	103.30(7)
O(1B)−V−S(1A)	88.24(5)	N(1B)−V−O(1A)	80.72(7)
N(1B)−V−S(1A)	81.72(5)	N(1B)−V−N(1A)	85.11(6)
O(1A)−V−N(1A)	85.28(7)	O(1A)−V−S(1A)	156.89(6)
N(1A)−V−S(1A)	78.36(5)	N(2B)−N(1B)−C(7B)	114.3(2)
N(1B)−C(7B)−S(1B)	112.4(2)	C(7B)−S(1B)−C(8B)	87.24(10)
S(1B)−C(8B)−N(2B)	114.7(2)	C(8B)−N(2B)−N(1B)	111.4(2)

deviations of S(1A), N(1A), O(1A), and O(1B) from the weighted least-squares plane being 0.0372, 0.0407, 0.0399, and 0.0364 Å, respectively. The two V−N bond distances are disparate; the axial V−N(1B) distance 2.342(2) Å is significantly elongated in compare to the equatorial V−N(1A) distance 2.114(2) Å, due to trans-labilizing influence of the terminal oxo group which forms angles in the range 94.07(8)−100.90(9)° with the basal plane. The trans angles O(1A)−V−S(1A) (156.89(6)°) and O(1B)−V−N(1A) (161.24(7)°) are somewhat compressed, giving evidence that the central vanadium is shifted slightly (by 0.2909 Å) out of the basal plane toward the apical oxo atom.

Perhaps the most interesting structural feature of this molecule is the formation of a heterocyclic thiadiazole ring. During the ring closure process, significant alterations take place in the bond lengths between most of the participating atoms. While the distances C(6B)−C(7B) (1.454(3) Å), C(7B)−N(1B) (1.309(3) Å), and N(2B)−C(8B) (1.300 (3) Å) are appreciably elongated, the N(1B)−N(2B) distance 1.380(2) Å on the other hand is substantially shortened compared to the corresponding distances C(6A)−C(7A) (1.425(3) Å), C(7A)−N(1A) (1.291(3) Å), N(2A)−C(8A) (1.287(3) Å), and N(1A)−N(2A) (1.413(3) Å) of the parent tridentate ligand (Table 2). The C(8)−S(1) distance 1.733(2) Å, however, remains the same before and after cyclization.

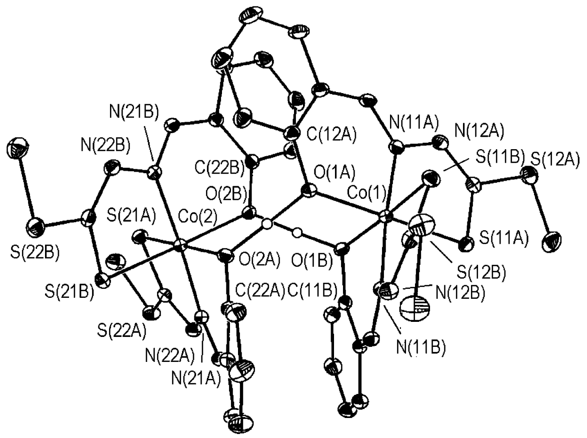

Figure 2. Molecular structure of [CoL^1(HL^1)]·H_2O (**2a**), showing the hydrogen-bonded dimeric form of the molecule. The ellipsoids represent the 30% probability level.

Table 3. Selected Bond Distances and Angles for [CoL^1(HL^1)]·H_2O (2a)

Distances (Å)			
Co(1)−N(11A)	1.907(2)	Co(2)−N(21A)	1.910(2)
Co(1)−N(11B)	1.909(2)	Co(2)−N(21B)	1.915(2)
Co(1)−O(1A)	1.9780(17)	Co(2)−O(2A)	1.9832(17)
Co(1)−O(1B)	1.9936(17)	Co(2)−O(2B)	1.9908(17)
Co(1)−S(11A)	2.2022(7)	Co(2)−S(21A)	2.2030(7)
Co(1)−S(11B)	2.1974(7)	Co(2)−S(21B)	2.1962(7)
O(1A)−C(12A)	1.354(3)	O(1B)−C(11B)	1.361(3)
O(2A)−C(22A)	1.358(3)	O(2B)−C(22B)	1.359(3)
Angles (deg)			
N(11A)−Co(1)−N(11B)	175.23(9)	N(21A)−Co(2)−N(21B)	176.66(9)
N(11A)−Co(1)−O(1A)	91.89(8)	N(21A)−Co(2)−O(2A)	90.79(8)
N(11B)−Co(1)−O(1A)	91.15(8)	N(21B)−Co(2)−O(2A)	90.20(8)
N(11A)−Co(1)−O(1B)	93.09(80)	N(21A)−Co(2)−O(2B)	92.26(8)
N(11B)−Co(1)−O(1B)	90.84(8)	N(21B)−Co(2)−O(2B)	91.00(8)
O(1A)−Co(1)−O(1B)	84.87(7)	O(2A)−Co(2)−O(2B)	85.45(7)
N(11A)−Co(1)−S(11B)	90.07(7)	N(21A)−Co(2)−S(21B)	90.68(6)
N(11B)−Co(1)−S(11B)	86.27(7)	N(21B)−Co(2)−S(21B)	86.13(6)
O(1A)−Co(1)−S(11B)	89.75(6)	O(2A)−Co(2)−S(21B)	90.09(5)
O(1B)−Co(1)−S(11B)	173.84(6)	O(2B)−Co(2)−S(21B)	174.69(6)
N(11A)−Co(1)−S(11A)	86.78(7)	N(21A)−Co(2)−S(21A)	86.60(6)
N(11B)−Co(1)−S(11A)	90.37(6)	N(21B)−Co(2)−S(21A)	92.59(6)
O(1A)−Co(1)−S(11A)	176.72(6)	O(2A)−Co(2)−S(21A)	175.89(6)
O(1B)−Co(1)−S(11A)	92.20(5)	O(2B)−Co(2)−S(21A)	91.48(5)
S(11B)−Co(1)−S(11A)	93.25(3)	S(21B)−Co(2)−S(21A)	93.11(3)

Hydrogen Bond Geometry

D−H···A	d(D−H), Å	d(H···A), Å	d(D···A), Å	D−H···A, deg
O(2A)−H(2A)···O(1A)	1.16(4)	1.29(4)	2.446(2)	177(3)
O(1B)−H(2B)···O(2B)	1.22(4)	1.25(4)	2.4748(19)	178(4)

[CoL^1(L^{1}H)]·H_2O. The molecular structure of **2a** is shown in Figure 2. Important metrical parameters are listed in Table 3. There are two molecules in the asymmetric unit. Each molecule has the composition [Co(L)(HL)]·H_2O (L = L^1) involving a ligand in completely deprotonated form (L^{2-}), and the second one (LH$^-$) that retains the proton attached to the phenolic oxygen. Interestingly, this proton helps to maintain the electroneutrality of the molecule and is involved in very strong hydrogen-bonding interactions with the phenoxide O atom of the adjoining molecule. The hydrogen atoms are approximately equidistant from the two O atoms, viz. O(1A) and O(2A) and O(1B) and O(2B), involved in the hydrogen bond (Figure 2). The O−H−O angles are close to 175° and the O···O separations are of ca. 2.4 Å, a situation somewhat analogous to the F−H−F case, observed in bifluoride ion.[25] The unit cell also contains one solvate water molecule/[Co(L)(LH)] unit.

The individual Co centers in this molecule have slightly distorted octahedral geometries completed by two molecules of the coordinated tridentate ligand, each contributing a set of S, N, and O donor atoms. For the geometry around the Co(1) center, the trans angles N(11A)−Co(1)−N(11B), O(1B)−Co(1)−S(11B), and O(1A)−Co(1)−S(11A) are 175.23(9), 173.84(6), and 176.72(6)°, respectively. Corresponding angles related to the Co(2) center are 176.66(9), 174.69(6), and 175.89(6)°, respectively. The bond angles between the cis ligands and the Co(1) center ranged from 93.25(3) to 84.87(7)°, the corresponding range for the Co(2) center being 93.11(3)−85.45(7)°. The average Co−N (1.910 Å) and Co−S bond distances (2.1997 Å) are not exceptional.[26] The average C−O$_{phen}$ bond distance of 1.358 Å indicates the existence of phenolate ligand and not the phenoxyl radical form.[27] Of particular interest are the Co−O$_{phen}$ distances in this molecule which vary in a quite narrow range, viz. 1.9780(17)−1.9936(17) Å (Table 3), that probably indicates identical electronic environment surrounding all the phenoxo O atoms, be they in the protonated or in the deprotonated forms. The extra proton of the LH$^-$ ligand is equally shared by both forms of the ligand, thus generating a unique hydrogen-bonded structure with two almost identical Co(III) centers. A similar type of dimeric structure has been reported recently for a cobalt(II) compound (Et$_4$N)[Co(mp)(Hmp)] (H$_2$mp = 2-mercaptophenol) where each Co(II) center has tetrahedral geometry joined together by analogous O−H−O hydrogen bonds.[28]

^{1}H NMR Spectroscopy. The ^{1}H NMR spectra of the complexes were recorded in CD$_2$Cl$_2$, and the details are presented in the Experimental Section. Two characteristic features in the free ligand spectrum (H$_2$L^1), one as a sharp singlet at 10.9 ppm and the other with a broad peak at 3.0 ppm due to phenolic OH and NH protons, respectively, are missing in the spectrum of **1a**. It displays a sharp singlet at 8.87 ppm because of the azomethyne proton with expected downfield shift due to complexation, compared to that of the free ligand (8.5 ppm). Appearance of a pair of strong singlets at 2.49 and 2.40 ppm due to SCH$_3$ protons and a number of multiplets in the aromatic region (7.80−6.78 ppm) are in conformity with the low symmetry of this molecule in solution due to the presence of both parent and cyclized forms of the ligand in this molecule.

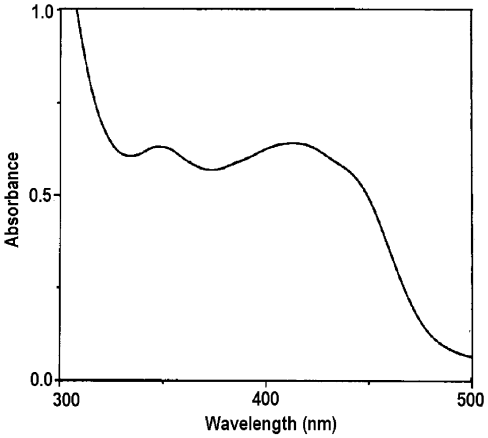

Figure 3. Electronic absorption spectrum of [CoL^2(HL^2)]·H$_2$O (**2b**) in methanol (concentrated 6.93 × 10^{-5} M).

Table 4. Electronic Spectral Data for the Complexes

complex	solvent	λ_{max}, nm (ϵ, mol^{-1} cm^2)
1a	CH$_2$Cl$_2$	495 (9700), 319 (4800), 281 (42 400)
1b	CH$_2$Cl$_2$	502 (9500), 320 (4900), 285 (39 600)
2a	CH$_3$OH	417 (8700), 348 (8900), 270 (36 500)
2b	CH$_3$OH	413 (8200), 343 (8600), 265 (32 100)

The spectrum of **2a** is simple and straightforward containing only a few signals, indicating higher symmetry of this molecule in solution than observed in the solid state. It involves a broad peak in the downfield (14.5 ppm) corresponding to a single proton due to a hydrogen-bonded O−H−O feature connecting both monoprotonated (LH$^-$) and deprotonated (L^{2-}) forms of the coordinated ligand. In addition, the spectrum shows a multiplet at 7.45 ppm (4H) and a strong singlet at 2.54 ppm (6H) due to aromatic and SCH$_3$ protons, respectively, as observed in **1a**. The other multiplet at 7.05 ppm accounts for six protons, four due to remaining aromatic ring protons and two for the azomethyne protons which undergo considerable upfield shift on complexation compared to **1a** as well as the free ligand as discussed above.

Optical Spectroscopy. The electronic absorption spectra of the complexes are summarized in Table 4. Vanadium(V) complexes (**1a,b**) display an intense broad peak centered at ca. 500 nm due to PhO$^-$ → V(dπ) LMCT transition.[29,30] The position of this LMCT band, as expected, is sensitive to the nature of the substituent in the *para* position of the coordinated phenoxo group.

Spectral features of the cobalt(III) complexes (**2a,b**) are dominated by the presence of a couple of bands in the near-UV region with moderate intensities. A representative spectrum for **2b** is shown in Figure 3. The lower energy band appearing at 413 nm with a long tail probably masks the weak spin-allowed d−d transitions expected to appear for low-spin pseudooctahedral cobalt(III) complexes.[31] These intense bands are indicative of LMCT transitions, probably originated from S → Co^{III} charge transfers as reported in the literature[32,33] for comparable systems.

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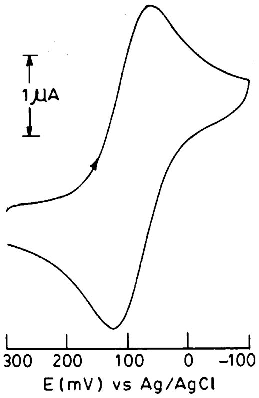

Figure 4. Cyclic voltammogram of **1b** in $CH_2Cl_2-CH_3CN$ (3:1 v/v) solution (containing 0.1 M TEAP) at a platinum disk electrode (scan rate 50 mV s^{-1} and potential recorded vs Ag/AgCl).

The remaining bands in the UV region for all the reported complexes are more likely to originate from intraligand transitions.

Electrochemistry. Cyclic voltammograms of the vanadium(V) complexes (**1a,b**) in $CH_2Cl_2-CH_3CN$ (3:1 v/v) solution have identical features. A representative voltammogram for **1b** is shown in Figure 4 which displays a one-electron reduction process corresponding to a V(V)/V(IV) electron transfer (eq 1). The $E_{1/2}$ values show a minor change from 0.10 to 0.11 V vs Ag/AgCl reference on going from **1a** to **1b**. On the basis of comparison with the ferrocenium/ferrocene couple (ΔE_p, 70 mV; i_{pc}/i_{pa}, 1 at 50 mV s^{-1}), the reduction process for **1b** (64 mV and 1.01 at 50 mV s^{-1}) is appropriately described as reversible, while the same process for **1a** (108 mV and 1.20 at 50 mV s^{-1}) is labeled quasi-reversible.[34] The single-electron stoichiometry of this process was further confirmed by controlled-potential coulometric experiments past the reduction process ($E_w = +0.04$ V vs Ag/AgCl) with **1b** ($n = 1.01 \pm 0.1$). The free ligands did not show any electrochemical response in the potential range -1.0 to $+1.0$ V vs Ag/AgCl reference.

$$[V^{V}OL(L_{cyclic})]^0 \underset{}{\overset{+e^-}{\rightleftharpoons}} [V^{IV}OL(L_{cyclic})]^- \qquad (1)$$

The Co(III) complexes (**2a,b**) are electrode inactive in the above potential range.

Concluding Remarks

The monooxovanadium(V) and the cobalt(III) complexes of dithiocarbazate ligands, described here, have some interesting similarities. In both the cases, during the preparation, the precursor metal ions (VO^{2+} and Co^{2+}) undergo one-electron oxidation to generate neutral complexes of VO^{3+} and Co^{3+} with 1:2 overall metal−ligand stoichiometry. The traditionally tridentate biprotic ligands[1−4] adopt here interesting and unprecedented means to neutralize the odd units of cationic charge to form neutral metal complexes.

In the vanadium(V) complexes (**1a,b**) one molecule of ligand coordinates in the customary fashion while the other undergoes a very interesting metal-induced intramolecular cyclization (Scheme 2) to form a bidentate monoanionic ligand with a coordinated thiadiazole moiety. Except for a suspected metal−redox link, we are at this stage unable to comment further on the mechanism of this interesting ligand-based cyclization reaction.

In the case of cobalt(III) complexes (**2a,b**), the molecules have a symmetric hydrogen-bonded dimeric structure in the solid state and possibly also in solution. Each ligand here virtually carries 1.5 units of negative charge with a proton shared equally by the two molecules of the dianionic ligands. In the solid state, this is confirmed by crystal structure analysis which reveals four almost equal $Co^{III}-O$ bonds (ranged between 1.9780(17) and 1.9936(17) Å) from the phenoxo donors. These bond lengths are appreciably longer than the conventional Co^{III}−phenoxo distances (1.860(2)−1.918(1) Å) reported in the literature.[35,36] This result provides further evidence of the equitable sharing of a single proton by the two phenoxo groups in the solid state. One can draw similar conclusion for the solution structure as well from ^1H NMR study.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of **1a** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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