Unprecedented Stabilization of Cobalt(II) in a Tetrahedral S_2O_2 Environment: The Use of a Redox-Noninnocent Ligand[†]

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The reaction of Zn(II) and Co(II) with thiosalicylic acid, *o*-HSC_6H_4COOH, and its methyl ester has led to the following complexes: $[Zn(SC_6H_4COO)]$ (**1**), $(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (**2**), $(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (**3**), $(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (**4**), $[Zn(SC_6H_4COOMe)_2]$ (**5**), and $[Co(SC_6H_4COOMe)_n]$, $n = 2$ (**6**), 3 (**7**). These ligands have not allowed stabilization of Co(II) in a sulfur−oxygen coordination environment. The structures of complexes **2**−**4** and **7** have been determined crystallographically. Those of **2**−**4** show significant similarities such as the behavior of the $^-SC_6H_4COO^-$ anion as chelating ligand and the involvement of sodium ions as a structural element. Thus, the structure of the $[Na\{Zn(SC_6H_4COO)_2\}(H_2O)]^-$ anion in complex **2** can be described as infinite chains of consecutive $[Zn(SC_6H_4COO)_2]^{2-}$ metalloligands linked by $[Na(H_2O)]^+$ centers, that of the $[Na\{Co(SC_6H_4COO)_3(H_2O)_2\}]_2^{4-}$ anion in **3** as a centrosymmetric tetranuclear Co_2Na_2 dimer with a $\{Co^{III}(S\cap O)_3\}Na(\mu\text{-}H_2O)_2Na\{Co^{III}(S\cap O)_3\}$ core, and that of the pentanuclear $[Na_3\{Co(SC_6H_4COO)_3\}_2(MeOH)_6]^{3-}$ anion in **4** as two dinuclear $[\{Co^{III}(S\cap O)_3\}Na(MeOH)_3]$ fragments linked to a central sodium ion, which appears to be the first structurally characterized example of a NaS_6 site. The use of the *o*-HSC_6H_4COOMe ligand allowed the synthesis of $[Co(SC_6H_4COOMe)_2]$ (**6**) but not its full structural characterization. Instead, $[Co(SC_6H_4COOMe)_3]$ (**7**) was obtained and structurally characterized. It consists of mononuclear molecules containing an octahedral $Co^{III}S_3O_3$ core. The selection of 2,2-diphenyl-2-mercaptoacetic acid as ligand with reductive properties has afforded the first mononuclear complex containing a $Co^{II}S_2O_2$ core and thus an unprecedented model for Co(II)-substituted metalloproteins containing tetrahedral MS_2O_2 active sites. The synthesis and full structural characterization of the isostructural complexes $(NEt_4)_2[Zn\{Ph_2C(S)COO\}_2]$ (**8**) and $(NEt_4)_2[Co\{Ph_2C(S)COO\}_2]$ (**9**) show that they consist of discrete $[M\{Ph_2C(S)COO\}_2]^{2-}$ anions, with a distorted tetrahedral coordination about the metal. In addition, the stability conferred by the ligand on the $Co^{II}S_2O_2$ core has allowed its characterization in solution by paramagnetic 1D and 2D ^1H NMR studies. The longitudinal relaxation times of the hyperfine-shifted resonances and NOESY spectra have led to the assignment of all resonances of the cobalt complex and confirmed that it maintains its tetrahedral geometry in solution. Magnetic measurements (2−300 K) for complex **9** and **9**$\cdot 2H_2O$ are in good agreement with distorted tetrahedral and octahedral environments, respectively.

Introduction

Substitution of the naturally occurring metals in metalloproteins is a common strategy in bioinorganic chemistry. Changing the native metal can provide valuable information on the structure and function of the metalloprotein. In some special cases, replacement of the metal ions is used to probe the metal site. Among the different transition-metal ions, Co(II) has been the most widely used as a substitute of the native metals mainly in zinc proteins, but also in copper, manganese, and iron proteins.[1] These ions are frequently bound to the protein through the histidyl, cysteinyl, and aspartic or glutamic acid residues and thus to nitrogen, sulfur, and oxygen atoms. The unique features of Co(II) allow many spectroscopic methods, such as UV−vis spectroscopy, and make it suitable for magnetic susceptibility measurements and paramagnetic NMR studies on cobalt(II)-substituted metalloproteins.

Cobalt(II) complexes with tetrahedral coordination are relatively abundant in the literature. However, it is well-known that the nature of the donor atoms plays a crucial role in the formation and further stability of the complex species. Thus, tetrahedral species containing $Co^{II}N_4$ and $Co^{II}N_2O_2$ cores do not usually require strict anaerobic conditions, those with $Co^{II}O_4$ and $Co^{II}S_4$, particularly the latter, oxidize very easily, and those with $Co^{II}S_xO_{4-x}$ are extremely sensitive to the presence of traces of oxygen.[2] In agreement with this behavior, studies on cobalt(II) thiolates of known structure are still very few,[3] and those relative to thiol ligands containing an additional oxygen-donor

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[†] Abbreviations: 1D and 2D, one-dimensional and two-dimensional; NOESY, nuclear Overhauser effect spectroscopy.

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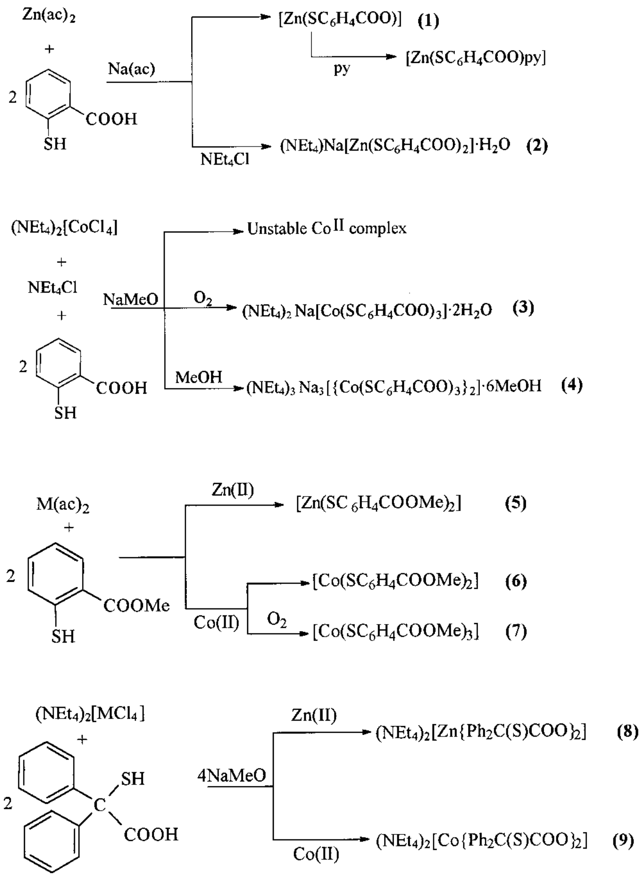
(1) (a) Bertini, I.; Gray, H. B.; Lippard, S. J.; Valentine, J. S. *Bioinorganic Chemistry*; University Science Books: Sausalito, CA, 1994. (b) Donaire, A.; Salgado, J.; Jiménez, H. R.; Moratal, J. M. In *Nuclear Magnetic Resonance of Paramagnetic Macromolecules*; La Mar, G. N., Ed.; Nato Series C: Mathematical and Physical Sciences, Vol. 457; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; pp 213−244 and references therein.

(2) Bertini, I.; Luchinat, C. *Advances in Inorganic Biochemistry*; Eichorn, G. L., Marzilli, L. G., Eds.; Elsevier: New York, 1984; pp 71−111.

10.1021/ic000223q CCC: \$19.00

Scheme 1



group reduce to only one example, $(NEt_4)_2[Co(mp)(Hmp)]_2$.[4] This binuclear complex of 2-mercaptophenol (H_2mp) dissociates in DMSO to its monomer, which is rapidly oxidized by traces of air.

As an extension of our ongoing work on thiol ligands containing an additional secondary function,[5] we designed different syntheses to obtain Co(II) tetrahedral complexes containing the $Co^{II}S_2O_2$ core. In all cases the thiol ligand included either a carboxylic acid or an ester as a second functional group. However, the use of chelating ligands, such as thiosalicylic acid and the corresponding methyl ester, under anaerobic conditions, did not lead to stable Co(II) complexes. Instead, the strategy of using as a ligand a compound with reducing properties, such as 2,2-diphenyl-2-mercaptoacetic acid, $Ph_2C(SH)COOH$, allowed the synthesis and full characterization in the solid state as well as in solution of the corresponding mononuclear Co(II) complex. In this paper, we report an extensive set of results for zinc and cobalt complexes of thiosalicylic acid, $[Zn(SC_6H_4COO)]$ (**1**), $(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (**2**), $(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (**3**), and $(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (**4**), its corresponding methyl ester, $[Zn(SC_6H_4COOMe)_2]$ (**5**) and $[Co(SC_6H_4COOMe)_n]$, $n = 2$ (**6**), 3 (**7**), and 2,2-diphenyl-2-mercaptoacetic acid, $(NEt_4)_2[M\{Ph_2C(S)COO\}_2]$, M = Zn (**8**), Co (**9**), including full synthetic (Scheme 1) and structural details. The structures of complexes **2**–**4** and **7**–**9** have been solved by X-ray diffraction. The polynuclear array of complexes **2**–**4** can be rationalized as coordination of sodium ions by 3d-metal complexes containing $\{Zn^{II}(S\cap O)_2\}$ or $\{Co^{III}(S\cap O)_3\}$ cores. The novel air-stable Co(II) complex **9** has allowed a detailed magnetic characterization as well as determination of its structure in solution by means of electronic UV–vis data and paramagnetic 1D and 2D ^1H NMR experiments. The significance of these results is that they show that the electronic properties of the ligand are essential for the stabilization of the highly oxidizable $Co^{II}S_2O_2$ core. We think that this knowledge could also be used to increase the stability of other thiolates with metals in low oxidation states.

Experimental Section

Materials and Methods. All operations were carried out under a pure dinitrogen atmosphere. All solvents were anhydrous and carefully degassed prior to use. In the synthesis of cobalt complexes the solvents were deoxygenated under nitrogen by several freeze–vacuum–thaw cycles and then saturated with argon. Thiosalicylic acid and its methyl ester were commercial samples (Sigma). According to ^1H and ^{13}C NMR data, the former contained minor impurities of the corresponding *meta* and *para* isomers. The 2,2-diphenyl-2-mercaptoacetic acid was obtained by published procedures.[6] Solutions of 2,2-diphenyl-2-mercaptoacetic acid in organic solvents at room temperature yield a blue solid, whose ^{13}C NMR spectrum shows the same signals as that of thiobenzophenone. The formation of the blue solid is greatly enhanced by heat. It is soluble in nonpolar solvents, from which it does not crystallize. If the solution is opened to the atmosphere, the color turns yellow and the IR spectrum of the isolated solid coincides with that of commercial benzophenone. These observations fully coincide with previous reports.[7] $Na_2[Ph_2C(S)COO]$ was generated in situ by adding the stoichiometric amount of NaMeO in MeOH to a solution of the acid in diethyl ether. $(Et_4N)_2[MCl_4]$, M = Zn, Co, were prepared as previously described.[8]

Elemental analyses were performed on a CE Instruments analyzer (C, H, N, S). IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer 1710 spectrophotometer. The electronic UV–vis spectra were performed on a diode array HP8452 spectrophotometer using a 1 cm quartz cell and with a 1.0 s integration time. Near-IR spectra were recorded on a NIRSystems 6500 spectrophotometer with an NR 6509 transmittance module and Perstorp Analytical NSAS v 3.30 control software. NMR spectra were recorded from solutions of complexes **1**–**8** in deuterated solvents using a Bruker AC250 or AM400 spectrometer. ^1H and ^{13}C chemical shift values were referenced to $SiMe_4$.

$[Zn(SC_6H_4COO)]$ (1). To a solution of 0.28 g (1.8 mmol) of HSC_6H_4COOH in 20 mL of ethanol was added a suspension of 0.25 g (1.8 mmol) of $NaCH_3COO$ in 10 mL of the same solvent. The solubilization of $NaCH_3COO$ as it reacted with the ligand made the mixture deepen its yellow color until it finally became a clear solution. Then, a solution of 0.20 g (0.9 mmol) of $Zn(CH_3COO)_2\cdot 2H_2O$ in warm ethanol was added with stirring, during which time a white solid appeared. This was filtered and washed with warm ethanol and ether, and dried, affording 0.06 g (32.3%) of pure product. Anal. Calcd for $C_7H_4O_2SZn$: C, 39.6; H, 2.145; S, 14.85. Found: C, 38.64; H, 1.84; S, 14.76. This complex is highly insoluble. It only dissolves in warm DMSO and pyridine, with which it reacts reversibly. Thus, the solution of $[Zn(SC_6H_4COO)]$ in pyridine yielded a white solid of different solubility than its precursor, whose analysis is suggestive of the solvate $[Zn(SC_6H_4COO)(py)]$. Anal. Calcd for $C_{13}H_9NO_2SZn$: C, 48.57; H, 3.26; N, 5.61; S, 9.76. Found: C, 48.58; H, 3.04; N, 4.75; S, 10.79. However, it reverted to $[Zn(SC_6H_4COO)]$ when dissolved in CH_2Cl_2 or $CHCl_3$. According to the yield of this reaction, the filtrate contained zinc (0.6 mmol) and excess ligand (1.5 mmol) if the initial 1:2 molar ratio was considered, and thus it was used as a starting material in the following synthesis.

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(3) (a) Dance, I. G. *Polyhedron* **1986**, *5*, 1037–1104. (b) Dance, I. G. In *Metallothioneins*; Stillman, M. J., Shaw, C. F., III, Suzuki, K. T., Eds.; VCH: New York, 1992; pp 328–330. (c) Okamura, T.; Takamizawa, S.; Ueyama, N.; Nakamura, A. *Inorg. Chem.* **1998**, *37*, 18–28.

(4) Kang. B.; Weng, L.; Liu, H.; Wu, D.; Huang, L.; Lu, C.; Cai, J.; Chen, X.; Lu, J. *Inorg. Chem.* **1990**, *29*, 4873–4877.

(5) González-Duarte, P.; Clegg, W.; Casals, I.; Sola, J.; Rius, J. *J. Am. Chem. Soc.* **1998**, *120*, 1260–1266.

(6) Buehler, C. A.; Smith, H. A.; Nayad, K. V.; Magee, T. A. *J. Org. Chem.* **1961**, *26*, 1573–1577.

(7) Cervilla, A.; Llopis, E. Personal communication.

(8) Gill, N. S.; Taylor, F. B. *Inorg. Synth.* **1967**, *9*, 136–142.

(NEt$_4$)Na[Zn(SC$_6$H$_4$COO)$_2$]·H$_2$O (2). In an attempt to prepare the $(NEt_4)_2[Zn(SC_6H_4COO)_2]$ complex, a solution of NEt_4Cl in ethanol was added to the filtrate of the previous synthesis. The amount of NEt_4Cl added was calculated on the basis of the zinc remaining in the filtrate and assuming that a 2:1 NEt_4^+:Zn(II) molar ratio was needed. An abundant white solid appeared almost immediately. The solvent was partially removed by vacuum and the solid filtered, washed with ether, and dried. The yield, based on the amount of zinc remaining in the mother solution of the previous synthesis, was 0.09 g, 26.62%. Anal. Calcd for $C_{22}H_{30}NO_5NaS_2Zn$: C, 48.30; H, 5.16; N, 2.41; S, 11.65. Found: C, 48.85; H, 5.55; N, 2.59; S, 11.84. Ether diffusion into a solution of this compound in acetonitrile/acetone gave suitable crystals for X-ray diffraction.

(NEt$_4$)$_2$Na[Co(SC$_6$H$_4$COO)$_3$]·2H$_2$O (3). To a suspension of 0.20 g (0.4 mmol) of $(Et_4N)_2[CoCl_4]$, 0.24 g (1.5 mmol) of HSC_6H_4COOH, and 0.22 g (1.3 mmol) of NEt_4Cl in 30 mL of ethanol at 0 °C was added slowly with stirring 0.6 mL (3.1 mmol) of NaMeO in 20 mL of ethanol. This addition was accompanied by a color change of the mixture from yellow to blue and the appearance of a solid. Immediately after filtration, washing, and drying, the solid was green, but it rapidly turned to black, indicating the oxidation of cobalt. The remaining deep blue filtrate was concentrated to dryness in a vacuum, the residue redissolved in acetonitrile at room temperature, and the solution filtered. While this solution was being stirred, it turned dark brown, despite many attempts to maintain strict control of the anaerobic conditions. After 2 days of stirring the solution was warmed to 50 °C and eventually left open to the atmosphere. The resulting black solid and the crystals obtained from the mother solution agree with the title compound. However, solution of the crystal structure revealed not only that oxidation had affected Co(II) totally but also that a fraction of thiolate ligands have converted into sulfinate. The assumption that one-third of the coordinated thiolate ligands, RS^-, had oxidized into sulfinate, RSO_2^-, afforded the best match between experimental and calculated analytical data. Anal. Calcd for $C_{37}H_{56}N_2O_{10}NaS_3Co$: C, 51.27; H, 6.46; N, 3.47; S, 11.08. Found: C, 51.27; H, 6.46; N, 3.23; S, 11.08.

(NEt$_4$)$_3$Na$_3$[{Co(SC$_6$H$_4$COO)$_3$}$_2$]·6MeOH (4). In a manner analogous to the preceding preparation, 0.4 mmol of $(Et_4N)_2[CoCl_4]$, 1.5 mmol of HSC_6H_4COOH, and 1.3 mmol of NEt_4Cl in 30 mL of ethanol were combined with 3.1 mmol of NaMeO in 10 mL of ethanol. The same change of color of the solution was observed, and again the isolated green solid turned to black. Immediately after filtration, the deep blue filtrate was concentrated to dryness, the residue redissolved in acetonitrile, and the solution filtered. To this solution were added 5 mL of MeOH and 5 mL of ether. After several days under nitrogen, the solution had kept its blue color and the crystals formed were suitable for X-ray diffraction. However, even though solution of the structure showed that cobalt(II) had oxidized and the title compound was the main product, analytical and X-ray data indicated the presence of some Co(II) ions. Anal. Calcd for $C_{72}H_{108}N_3O_{18}Na_3S_6Co_2$: C, 48.51; H, 6.30; N, 2.68; S, 11.7. Found: C, 51.39; H, 6.42; N, 2.50; S, 11.42.

[Zn(SC$_6$H$_4$COOMe)$_2$] (5). To a solution of 0.25 mL (1.8 mmol) of HSC_6H_4COOMe in 8 mL of ethanol at room temperature was added slowly with stirring 0.2 g (0.9 mmol) of $Zn(CH_3COO)_2·2H_2O$ in 23 mL of warm ethanol, during which time the solution deepened its initially yellow color. Stirring was continued until formation of an abundant solid. The reaction mixture was concentrated to ca. 25 mL, and the yellow solid was filtered, washed with warm ethanol, and dried; yield 0.29 g, 80%. Despite the solubility of the solid in CH_2Cl_2 and $CHCl_3$, attempts to obtain single crystals were unsuccessful. Anal. Calcd for $C_{16}H_{14}O_4S_2Zn$: C, 48.07; H, 3.50; S, 16.025. Found: C, 48.20; H, 3.60; S, 16.12.

[Co(SC$_6$H$_4$COOMe)$_n$], $n = 2$ (6), 3 (7). The following manipulations were carried out under argon. To a solution of 0.22 mL (1.6 mmol) of HSC_6H_4COOMe in 8 mL of ethanol at room temperature was added slowly with stirring 0.20 g (0.8 mmol) of $Co(CH_3COO)_2·4H_2O$ in 15 mL of ethanol, during which time the solution changed its color from yellow to brown-green. The addition of the metal was concomitant with the formation of an orange solid, which was eventually filtered and dried. Analytical data for this solid agree well with $[Co(SC_6H_4COOMe)_2]$ (**6**). Anal. Calcd for $C_{16}H_{14}O_4S_2Co$: C, 48.85; H, 3.56; S, 16.28. Found: C, 48.35; H, 3.20; S, 16.25. Although the complex is soluble in most organic solvents, attempts to obtain crystals were hindered by the ease of oxidation of Co(II) in solution.

The previous filtrate afforded dark green microcrystals, which were recrystallized in diethyl ether under an open atmosphere. Analytical and X-ray diffraction data showed that this solid corresponds to $[Co(SC_6H_4COOMe)_3]$ (**7**). Anal. Calcd for $C_{24}H_{21}O_6S_3Co$: C, 51.43; H, 3.75; S, 17.14. Found: C, 51.07; H, 3.67; S, 17.41.

(NEt$_4$)$_2$[Zn{Ph$_2$C(S)COO}$_2$] (8). To 5 mL of a 0.16 M solution (0.8 mmol) of $Ph_2C(SH)COOH$ in diethyl ether was added 5 mL of a 0.32 M solution of NaMeO (1.6 mmol) in methanol. To this solution was added dropwise 14 mL of a 0.03 M solution (0.4 mmol) of $(Et_4N)_2[ZnCl_4]$ in acetonitrile. After 30 min of stirring, the solvent was removed, and the residue was extracted with the minimum amount of acetonitrile. To the filtrate from the acetonitrile suspension was added diethyl ether until separation of microcrystals, yield 0.16 g, 48%. Anal. Calcd for $C_{44}H_{60}N_2O_4S_2Zn$: C, 65.23; H, 7.41; N, 3.46; S, 7.90. Found: C, 63.73; H, 7.50; N, 3.49; S, 7.83. Recrystallization of this solid from acetonitrile by ether diffusion under a nitrogen atmosphere afforded colorless crystals.

Acetonitrile solutions of this complex developed a very light blue color after several hours of their preparation. This solution turned yellow if opened to the atmosphere. These findings were indicative of the oxidation of a small fraction of the coordinated 2,2-diphenyl-2-mercaptoacetic acid ligand to thiobenzophenone, which in turn oxidizes to benzophenone in the presence of oxygen. This decomposition was also accompanied by the appearance of an unidentified solid residue.

(NEt$_4$)$_2$[Co{Ph$_2$C(S)COO}$_2$] (9). This preparation followed closely that of the zinc(II) analogue, and employed $Ph_2C(SH)COOH$ (0.8 mmol), sodium methoxide in methanol (1.6 mmol), and $(Et_4N)_2[CoCl_4]$ (0.4 mmol). The deep blue filtrate was concentrated to dryness in a vacuum, the residue redissolved in acetonitrile, and the solution filtered. Ether was added until crystallization began; yield 0.19 g, 60%. Anal. Calcd for $C_{44}H_{60}N_2O_4S_2Co$: C, 65.75; H, 7.47; N, 3.48; S, 7.97. Found: C, 62.75; H, 7.44; N, 3.39; S, 7.62. The compound was recrystallized by ether diffusion into the acetonitrile solution under nitrogen, giving deep blue crystals.

Unlike the Zn analogue, the light blue color indicating the oxidation of the coordinated ligand in solutions of $(NEt_4)_2[Co\{Ph_2C(S)COO\}_2]$ to thiobenzophenone could not be visually observed because of the intense blue color of the cobalt complex. However, a multiplet centered at 8 ppm in the ^1H NMR spectrum of the complex in CD_3CN indicated the presence of aromatic protons unaffected by the Co(II) paramagnetic ion. As the presence of this cation only alters the chemical shift of the protons of coordinated ligands, the signal at 8 ppm and the appearance of a small solid residue were both indicative of a minor oxidative decomposition of the ligand. In this case the ^{13}C NMR spectrum of the solution could not be recorded because of the presence of the Co(II) ion.

Collection and Reduction of X-ray Data for Complexes 2−4 and 7−9. A summary of crystal data, data collection, and refinement parameters for the six structural analyses is reported in Table 1. Crystals were examined on a Bruker AXS SMART CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and low-temperature equipment operating at 160 K. Cell constants were obtained from a least-squares fit on the observed setting angles of all significant intensity reflections. Intensities were integrated from a series of 0.3° ω rotation frames covering at least a hemisphere of reciprocal space, and were corrected for absorption by semiempirical methods based on redundant and symmetry-equivalent reflections.[9]

The structures were solved by direct methods and were refined by full-matrix least-squares on all unique F^2 values, with anisotropic displacement parameters for non-hydrogen atoms and with isotropic H atoms constrained with a riding model.[10] Disorder, particularly of tetraethylammonium cations, was resolved in several of the structures and was successfully refined with the aid of restraints on geometry and displacement parameters. For the noncentrosymmetric structure of

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(9) Sheldrick, G. M. *SADABS*; Bruker AXS: Madison, WI, 1997.

(10) Sheldrick, G. M. *SHELXTL*, Version 5; Bruker AXS: Madison, WI, 1994.

Table 1. Crystal Data and Data Collection and Refinement for Complexes **2**, **3**, **4**, **7**, **8**, and **9**

	2	**3**	**4**	**7**	**8**	**9**
empirical formula	$C_{22}H_{30}NNaO_5S_2Zn$	$C_{74}H_{112}Co_2N_4Na_2O_{16}S_6{}^c$	$C_{72}H_{108}Co_2N_3Na_3O_{18}S_6$	$C_{24}H_{21}CoO_6S_3$	$C_{44}H_{60}ZnN_2O_4S_2$	$C_{44}H_{60}CoN_2O_4S_2$
fw	541.0	1669.9	1682.8	560.5	810.4	804.0
cryst size, mm	0.62 × 0.20 × 0.20	0.76 × 0.62 × 0.46	0.50 × 0.50 × 0.40	0.50 × 0.34 × 0.28	0.50 × 0.48 × 0.32	0.60 × 0.60 × 0.60
space group	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)	$R\bar{3}$ (no. 148)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a, Å	7.8669(10)	12.1680(2)	16.3925(13)	7.7256(14)	14.2372(11)	14.2439(10)
b, Å	14.358(2)	17.9288(2)	16.3925(13)	11.141(2)	18.7351(14)	18.7125(13)
c, Å	21.503(3)	19.1155(2)	58.502(5)	15.606(3)	17.1012(13)	17.1556(11)
α, deg	90	90	90	103.105(5)	90	90
β, deg	90	92.659(2)	90	99.194(5)	112.658(2)	112.826(2)
γ, deg	90	90	120	104.501(4)	90	90
V, Å^3	2428.8(5)	4165.70(6)	13614(2)	1232.8(4)	4209.4(6)	4214.5(5)
Z	4	2	6	2	4	4
ρ_{calcd}, g cm^{-3}	1.479	1.330	1.232	1.510	1.279	1.267
μ, cm^{-1}	12.3	6.2	5.8	9.9	7.3	5.5
$R(F)$ ($F^2 \geq 2\sigma(F^2)$)^a	0.0335	0.0671	0.0548	0.0403	0.0767	0.0937
$R_w(F^2)$ (all data)^b	0.0752	0.2054	0.1573	0.1022	0.1864	0.2468

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F^2) = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$. ^{c} Ignoring the partial ligand oxidation.

complex **2**, the absolute configuration was determined by refinement of the Flack parameter to 0.028(12).[11]

The main bond distances and angles for complexes **2**−**4** and **7**−**9** are given in Table 2.

Physical Techniques. ^1H NMR experiments for complex **9** in solution were performed on a Varian Unity 400 spectrometer. One-dimensional spectra were recorded in CD_3CN solvent with presaturation of the CH_3CN signal during part of the relaxation delay. Presaturation times of 50−100 ms, acquisition times of 20−100 ms, 10−100 kHz spectral widths, and relaxation delay times of 50−100 ms were used. 1D spectra were processed using exponential line-broadening weighting functions with values of 20−40.

Data for nonselective longitudinal relaxation times were determined using the inversion-recovery pulse sequence[12] d_1−180°−τ−90°−*Acq*, 20 values of τ were selected, $d_1 + Acq$ values were at least 5 times the longest expected T_1, and the number of scans was 128. The T_1 values were calculated from the inversion−recovery equation.

NOESY experiments were performed in the hypercomplex (States−Haberkorn) mode.[13] Because the ^1H relaxation times were diverse, 2D spectra were recorded using a wide range of conditions. A total of 256−512 t_1 increments, 256−1024 scans, 512−1024 points in the t_2 dimension, 15−50 kHz spectral widths in both dimensions, acquisition times of 10−20 ms, and relaxation delays of 10−120 ms were used. The mixing time for NOESY ranged from 0.6 to 10 ms. Additionally, different processing conditions were also used. NOESY spectra were Fourier transformed using square sine bell weighting functions shifted 45°, 60°, or 75°, depending on the paramagnetic character of the observed signals. The number of points used for processing was 512, 1024, or 2048 in both dimensions. NOESY spectra were baseline corrected. NMR data were processed on a SUN Sparc 5 station using the VNMRX 4.3B program.

Magnetic susceptibility measurements (2.0−300 K) for complex **9** were carried out with a Quantum Design SQUID magnetometer under an applied magnetic field of 1 T at high temperature ($T > 10$ K) and only 50 G at low temperature ($T < 10$ K) to avoid any problem of magnetic saturation. The device was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$. The corrections for the diamagnetism and temperature-independent paramagnetism (tip) for **9** were estimated to be -400×10^{-6} and 500×10^{-6} cm^3 mol^{-1}, respectively.

Results and Discussion

Synthesis of the Complexes. The approach of using thiosalicylic acid, *o*-HSC_6H_4COOH, and its methyl ester, *o*-HSC_6H_4COOMe, as potential ligands to obtain isostructural Zn(II) and Co(II) species did not yield the desired complexes. Several Zn(II) complexes were obtained, but apparently these ligands cannot overcome the low stability of Co(II) complexes involving simultaneous coordination to oxygen and sulfur atoms. However, 2,2-diphenyl-2-mercaptoacetic acid, $Ph_2C(SH)COOH$, gave satisfactory results. A summary of the reaction procedures and corresponding products is given in Scheme 1. ^1H and ^{13}C NMR parameters of the free ligands and complexes **1**−**8** allowed their characterization and showed that in all complexes ligands become equivalent in solution, but they did not provide information on structural details, such as the coordination mode of the carboxylate group. Assignments of the IR bands corresponding to the main carboxylate and carbonyl stretching frequencies in the solid complexes were based on literature data.[14] However, due to the complexity of the spectra of the heterobimetallic zinc−sodium (**2**) and cobalt−sodium (**3**, **4**) complexes in the region 1600−1200 cm^{-1}, definite assignments of the carboxylate stretching vibrations required previous knowledge of the structure and were only possible for the latter two. The electronic absorptions of the d−d transitions for the cobalt(II) (**9**) and cobalt(III) (**3**, **4**, **7**) complexes in solution are in good agreement with the coordination geometry found in the solid phase. NMR, IR, and UV−vis data are given in the Supporting Information. The molecular structures of complexes $(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (**2**), $(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (**3**), $(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (**4**), $[Co(SC_6H_4COOMe)_3]$ (**7**), and $(NEt_4)_2[M\{Ph_2C(S)COO\}_2]$, where M = Zn (**8**) or Co (**9**), are described below. In addition, the magnetic features and corresponding electronic states of the Co(II) complex **9** in the solid phase and a detailed analysis of its structure in solution by paramagnetic 1D and 2D ^1H NMR studies are also reported.

Consideration of the Zn(II) complexes $[Zn(SC_6H_4COO)]$ (**1**), $(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (**2**), and $[Zn(SC_6H_4COOMe)_2]$ (**5**) indicates a different behavior of the thiosalicylic acid and its methyl ester as ligands. The former is totally deprotonated under our experimental conditions, as shown in the IR spectra of **1** and **2** by the absence of bands in the region denoting hydrogen-bonded carboxylic acids (3200−2500 cm^{-1}). For both ligands, there is no absorption corresponding to the S−H stretching vibration (ca. 2600 cm^{-1}). Thus, the charge of the thiosalicylate anion, −2, agrees with the formation of **1**, whose very low solubility is indicative of a polymeric structure. The IR spectrum of this complex indicates a chelating and bridging behavior of the carboxylate group and thus reinforces the previous suggestion. Excess ligand together with the presence

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(11) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.

(12) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987.

(13) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286−92.

(14) Deacon, G. B.;. Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2**−**4** and **7**−**9**[a]

Complex 2			
Zn−O(11)	1.953(3)	Zn−O(21)	1.994(2)
Zn−S(1)	2.2571(10)	Zn−S(2)	2.2779(10)
Na−O(11)	2.407(3)	Na−O(12)	2.498(3)
Na−O(22A)	2.338(3)	Na−O(3)	2.349(3)
Na−O(21B)	2.404(3)	Na−O(22B)	2.576(3)
O(11)−Zn−O(21)	103.92(11)	O(11)−Zn−S(1)	98.70(8)
O(21)−Zn−S(1)	118.52(8)	O(11)−Zn−S(2)	112.48(8)
O(21)−Zn−S(2)	94.53(8)	S(1)−Zn−S(2)	127.30(4)
O(22A)−Na−O(3)	106.42(11)	O(22A)−Na−O(21B)	110.79(10)
O(3)−Na−O(21B)	102.15(11)	O(22A)−Na−O(11)	103.48(10)
O(3)−Na−O(11)	89.62(11)	O(21B)−Na−O(11)	138.45(10)
O(22A)−Na−O(12)	88.70(9)	O(3)−Na−O(12)	142.11(11)
O(21B)−Na−O(12)	104.47(10)	O(11)−Na−O(12)	52.74(9)
O(22A)−Na−O(22B)	159.43(9)	O(3)−Na−O(22B)	90.28(10)
O(21B)−Na−O(22B)	52.54(8)	O(11)−Na−O(22B)	88.22(10)
O(12)−Na−O(22B)	85.04(9)		
Complex 3			
Co−O(3)	1.953(3)	Co−O(5)	1.963(3)
Co−O(1)	1.982(3)	Co−S(3)	2.1982(11)
Co−S(1)	2.2033(11)	Co−S(2)	2.2160(11)
Na−O(1)	2.414(3)	Na−O(3)	2.396(3)
Na−O(5)	2.381(3)	Na−O(8)	2.300(4)
Na−O(7A)	2.368(3)	Na−O(7)	2.374(3)
O(3)−Co−O(5)	84.73(11)	O(3)−Co−O(1)	83.89(11)
O(5)−Co−O(1)	82.79(11)	O(3)−Co−S(3)	93.66(9)
O(5)−Co−S(3)	91.15(8)	O(1)−Co−S(3)	173.63(9)
O(3)−Co−S(1)	173.85(9)	O(5)−Co−S(1)	92.87(9)
O(1)−Co−S(1)	90.20(9)	S(3)−Co−S(1)	92.05(5)
O(3)−Co−S(2)	91.10(9)	O(5)−Co−S(2)	175.32(8)
O(1)−Co−S(2)	94.67(9)	S(3)−Co−S(2)	91.24(4)
S(1)−Co−S(2)	91.07(4)	O(8)−Na−O(7A)	93.4(2)
O(8)−Na−O(7)	104.6(2)	O(7A)−Na−O(7)	86.32(11)
O(8)−Na−O(5)	142.4(2)	O(7A)−Na−O(5)	123.99(12)
O(7)−Na−O(5)	83.58(11)	O(8)−Na−O(3)	81.19(13)
O(7A)−Na−O(3)	141.93(12)	O(7)−Na−O(3)	131.60(12)
O(5)−Na−O(3)	67.08(10)	O(8)−Na−O(1)	119.8(2)
O(7A)−Na−O(1)	84.74(11)	O(7)−Na−O(1)	135.07(12)
O(5)−Na−O(1)	65.92(10)	O(3)−Na−O(1)	66.31(10)
Complex 4			
Co−O(1)	1.972(2)	Co−S	2.2215(8)
Na(1)−S	2.8171(7)	Na(2)−O(3)	2.350(3)
Na(2)−O(1)	2.435(3)	O(1)−Na(2)−O(1A)	65.92(9)
O(1A)−Co−O(1)	84.41(9)	O(1A)−Co−S	93.60(6)
O(1)−Co−S	90.61(6)	O(1)−Co−S(A)	174.78(7)
S−Co−S(A)	91.24(3)	S(A)−Na(1)−S	68.61(2)
O(3A)−Na(2)−O(3)	99.57(10)	O(3A)−Na(2)−O(1)	140.27(10)
O(3)−Na(2)−O(1)	80.57(8)	O(3)−Na(2)−O(1A)	119.74(9)
Complex 7			
Co−O(21)	1.950(2)	Co−O(31)	1.960(2)
Co−O(11)	1.980(2)	Co−S(2)	2.1822(9)
Co−S(1)	2.1853(9)	Co−S(3)	2.1962(9)
O(21)−Co−O(31)	83.90(9)	O(21)−Co−O(11)	83.26(9)
O(31)−Co−O(11)	83.64(9)	O(21)−Co−S(2)	95.05(7)
O(31)−Co−S(2)	177.17(7)	O(11)−Co−S(2)	93.63(7)
O(21)−Co−S(1)	176.87(7)	O(31)−Co−S(1)	93.47(7)
O(11)−Co−S(1)	94.78(7)	S(2)−Co−S(1)	87.50(4)
O(21)−Co−S(3)	93.47(7)	O(31)−Co−S(3)	93.40(7)
O(11)−Co−S(3)	175.79(7)	S(2)−Co−S(3)	89.28(4)
S(1)−Co−S(3)	88.37(4)		

Complexes **8** and **9**

	M = Zn (**8**)	M = Co (**9**)		M = Zn (**8**)	M = Co (**9**)
M−O(1)	1.976(4)	1.958(4)	M−S(1)	2.288(2)	2.283(2)
M−O(3)	1.998(3)	1.980(3)	M−S(2)	2.2584(15)	2.2483(15)
O(1)−M−O(3)	106.2(2)	109.7(2)	O(1)−M−S(1)	88.99(14)	87.24(14)
O(1)−M−S(2)	114.28(14)	115.69(14)	O(3)−M−S(1)	123.81(11)	126.29(11)
O(3)−M−S(2)	90.02(10)	88.53(10)	S(2)−M−S(1)	132.70(6)	130.33(6)

[a] Symmetry transformations used to generate equivalent atoms (labeled A and B) are given in the Supporting Information.

of NEt_4^+ counterions in the reaction medium led to the formation of the $[Zn(SC_6H_4COO)_2]^{2-}$ complex. According to X-ray data, this contains a tetrahedral ZnS_2O_2 core, but it does not exist as a discrete species in the solid state. The structure of (NEt_4)Na-

$[Zn(SC_6H_4COO)_2]$ (**2**) is polymeric and can be viewed as involving coordination of Na^+ by the carboxylate function of the $[Zn(SC_6H_4COO)_2]^{2-}$ metalloligands.

Replacement of the carboxylic acid in *o*-HSC_6H_4COOH by a methyl ester group led to a monoanionic ligand, which afforded an uncharged $[Zn(SC_6H_4COOMe)_2]$ (**5**) complex. Its very high solubility in most solvents was indicative of a mononuclear structure probably involving a ZnO_2S_2 core. This assumption is in accordance with the infrared data, which show that the ester ligand is bound to the metal through the thiolate sulfur and the carbonyl ester group. Unfortunately, the high solubility of the complex made the attempts for obtaining single crystals unsuccessful.

As indicated above, the thiosalicylic acid and its methyl ester did not lead to stable Co(II) complexes. These proved to be extremely sensitive, particularly in solution, to even trace amounts of oxygen. Attempts to avoid decomposition by running the reaction at low temperature and by isolating the products within hours of their preparation were not successful in the case of the thiosalicylato ligand. They allowed the synthesis of $[Co(SC_6H_4COOMe)_2]$ (**6**), but its full structural characterization could not be achieved. Instead, several Co(III) complexes, $(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (**3**), $(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (**4**), and $[Co(SC_6H_4COOMe)_3]$ (**7**), were obtained and structurally characterized by X-ray diffraction. According to our reaction procedures, which were aimed at the synthesis of Co(II) complexes, the yields associated with the Co(III) complexes **3**, **4**, and **7**, as well as that of **6**, are not representative, and thus they have been omitted. In the three Co(III) compounds **3**, **4**, and **7**, the S_3O_3 coordination environments about Co(III) are closely similar, although only the structure of the last complex consists of mononuclear entities. Electronic spectral properties of these complexes in solution indicate that the $Co^{III}S_3O_3$ core is maintained and agree well with literature data for Co(III) species with octahedral S_6 or O_6 environments.[15] All these results led us to the conclusion that the chelate effect of a six-membered ring and the steric protection of the phenyl group of the previous ligands were not adequate either to obtain mononuclear Zn(II) complexes or to compensate for the ease of oxidation of Co(II) in a tetrahedral S_2O_2 environment.

Our next step was the selection of a new ligand, which should overcome the drawbacks found with *o*-HSC_6H_4COOH and *o*-HSC_6H_4COOMe. To this end, priority was given to the following requirements: the organic compound should have reductive properties in nonaqueous solutions, it should give rise to greater steric effects than the ligands previously investigated, and its coordination to a metal should lead to formation of a five- instead of a six-membered chelate ring. Structural and electrochemical data on several molybdenum complexes of 2,2-diphenyl-2-mercaptoacetic acid indicated that this compound could fulfill all the previous conditions.[16] Its ability to act as a reductant[17] seemed to be particularly interesting to overcome the difficulties found. Accordingly, the choice of $Ph_2C(SH)COOH$ allowed the synthesis of the Zn(II) and Co(II) complexes of formula $(NEt_4)_2[M\{Ph_2C(S)COO\}_2]$ by a straightforward procedure, as shown in Scheme 1. They proved to be isostructural, containing mononuclear $M^{II}S_2O_2$ distorted tetrahedral cores. Crystals of the $(NEt_4)_2[Co\{Ph_2C(S)COO\}_2]$ complex (**9**) showed no signs of alteration after 3 months under a nitrogen atmosphere. However, the intensely blue color of **9** turned to pale pink as the solid complex was left standing under an open atmosphere for several weeks. Magnetic measurements were indicative of the formation of an octahedral cobalt(II) complex of formula $\mathbf{9}\cdot 2H_2O$. Heating this hydrated form at 50 °C under vacuum yielded the original anhydrous complex **9**. The stability conferred by the ligand on the $Co^{II}S_2O_2$ core is not limited to the solid phase, but as described below, it also allowed the characterization of **9** in solution by paramagnetic 1D and 2D ^1H NMR studies.

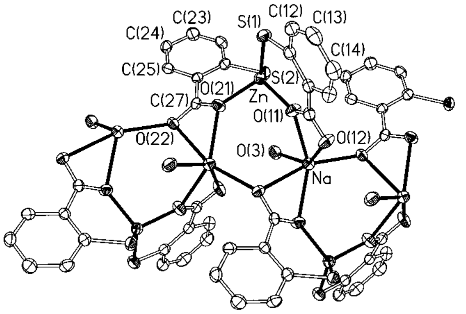

Figure 1. View of a section of the polymeric anion chain of complex **2**. Here and in other figures, displacement ellipsoids are at the 50% probability level and are shaded for non-carbon atoms, and unique atoms are labeled (some obscured labels are omitted in some figures). Hydrogen atoms are omitted. Bonds to metals are shown solid, others hollow.

In our opinion, the main feature of $Ph_2C(SH)COOH$ to achieve the stabilization of Co(II) in an S_2O_2 environment is its oxidative decomposition, which gives rise to a reductive atmosphere. This takes place according to a sequence of reactions which eliminate the traces of oxygen and involve formation of thiobenzophenone first and eventually benzophenone. Moreover, a minor solid residue observed in the solutions of this compound could include elemental sulfur. Overall, the use of a redox-noninnocent ligand has provided the characteristics required to generate efficiently (60% yield) an otherwise highly unstable complex species.

Molecular Structures. Zn(II) and Co(III) Complexes of Thiosalicylic Acid: $(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (2), $(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (3), and $(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (4). The structures of these complexes show significant similarities: (a) the ligand chelates the transition-metal centers through the thiolate sulfur and one of the oxygen atoms of the carboxylate group, yielding $\{Zn^{II}(S\cap O)_2\}$ and $\{Co^{III}(S\cap O)_3\}$ cores, (b) the sodium ions are involved in linking these zinc or cobalt species into more complicated frameworks, and (c) solvent molecules are included within the sodium coordination sphere.

$(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (2). The structure of this complex consists of $[Na\{Zn(SC_6H_4COO)_2\}(H_2O)]^-$ anions and NEt_4^+ cations. The former show a polymeric structure, which can be regarded as infinite chains of consecutive ZnS_2O_2 and NaO_6 sites, Figure 1. Alternatively, they can be considered as formed by $[Zn(SC_6H_4COO)_2]^{2-}$ metalloligands linked by $[Na(H_2O)]^+$ centers. The chains run parallel to each other and to the *x* axis and are well separated by NEt_4^+ counterions. The unit cell repeat for the chain includes two zinc and two sodium sites.

Coordination about the only crystallographically unique zinc is distorted tetrahedral. The distortion is essentially due to the bite angle of the ligands, 94.53(8)° and 98.70(8)°, which chelate the zinc atom by means of the thiolate sulfur and the oxygen

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(15) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; pp 463−478.

(16) Cervilla, A.; Ramírez, J. A.; Llopis, E.; Palanca, P. *Inorg. Chem.* **1993**, *32*, 2085−2091.

(17) Cervilla, A.; Llopis, E.; Domenech, A.; Ribera, A.; Palanca, P.; Gómez-Romero, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1005−1008.

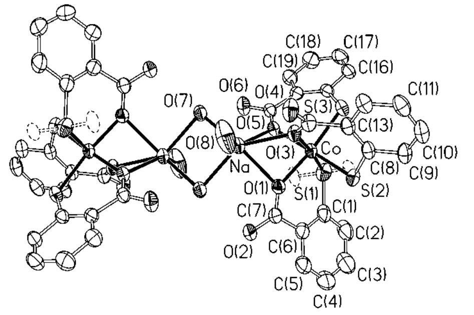

Figure 2. View of the centrosymmetric tetranuclear anion assembly in complex **3**. Partially occupied oxygen atom sites are shown dashed.

atom of a “unidentate” carboxylate group. These ligands are further involved in coordination, each carboxylate chelating a different sodium ion. The Zn−S and Zn−O bond distances average 2.268 and 1.974 Å. They are very close to those found in the mononuclear $[Zn\{Ph_2C(S)COO\}_2]^{2-}$ anion of complex **8** described below.

The crystallographically unique sodium is six-coordinate to five oxygen atoms from three carboxylate groups (Na−O distances range between 2.338 and 2.576 Å) and to one oxygen from a terminal H_2O ligand (Na−O distance 2.349 Å). As shown in Figure 1, each carboxylate group involved in the NaO_6 site comes from a different $[Zn(SC_6H_4COO)_2]^{2-}$ unit and shows a particular binding mode. One $-COO^-$ is only chelating, another one is chelating and bridging to a further sodium, and the third one behaves as unidentate in the NaO_6 site and bridges to another sodium, to which it also chelates. Overall, the carboxylate contacts to sodium ions give rise to Na_2ZnO_3 rings; these constitute the basic framework of the infinite chains, sharing their Na sites.

In the NaO_6 site, the Na−O distances agree well with those found for the same site in the $(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (**3**) and $(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (**4**) complexes here described and with those of related examples.[17−19] The geometry around sodium in $[Na\{Zn(SC_6H_4COO)_2\}(H_2O)]^-$ is very distorted, mainly caused by the chelating carboxylate ligands (average, 53°). However, considerable degrees of distortion are usual in Na six-coordinate geometries.[20] This geometric flexibility is a consequence of the nondirectional electrostatic nature of the interaction between Na^+ and donor atoms. For this reason, it imposes no constraints on the overall structure of the coordination framework.

$(NEt_4)_2Na[Co(SC_6H_4COO)_3]\cdot 2H_2O$ (3). The structure of this complex consists of discrete $[Na\{Co(SC_6H_4COO)_3(H_2O)_2\}]_2{}^{4-}$ anions, disordered $NEt_4{}^+$ cations, and disordered solvent molecules. The anion can be described as a centrosymmetric tetranuclear Co_2Na_2 dimer with a $\{Co^{III}(S{\cap}O)_3\}Na(\mu\text{-}H_2O)_2\text{-}Na\{Co^{III}(S{\cap}O)_3\}$ core, Figure 2. This framework can be viewed as being made up of metalloligands, each linked to one sodium ion of the central $Na(\mu\text{-}H_2O)_2Na$ unit. The crystallographic inversion center in the middle of the Na_2O_2 ring allows consideration of the anion as a dimer with crystallographically unique cobalt and sodium sites.

In the $\{Co(SC_6H_4COO)_3\}^{3-}$ unit, Co(III) is octahedrally coordinated to three chelating ligands. Each of these is bound to the metal center through the thiolate sulfur and one oxygen atom of the carboxylate group. The bite angle in the three ligands is very close to 90°, and the full set of angles about Co range between 82.8° and 94.7°. Coordinating sulfur and oxygen atoms occupy facial positions about the metal ion. The Co−O bonds average 1.96 Å, while Co−S bonds average 2.20 Å. These values agree well with those found in the other Co(III) complexes reported here. A comparison of the main geometric parameters of the $Co^{III}S_3O_3$ site in complex species $[Na\{Co(SC_6H_4COO)_3(H_2O)_2\}]_2{}^{4-}$, $[Na_3\{Co(SC_6H_4COO)_3\}_2(MeOH)_6]^{3-}$, and $[Co(SC_6H_4COOMe)_3]$ (**7**), Table 2, shows that they are structurally very similar and compare well with literature data.[21−25]

The sodium is six-coordinated by oxygen atoms. Three oxygen donors are derived from the carboxylate groups of the $^-SC_6H_4COO^-$ ligands. The three oxygen atoms that define one face of the octahedron about Co in the CoS_3O_3 site are μ-bridging between cobalt and sodium. The exocyclic oxygens of the carboxylate groups are not involved in coordination. Two further oxygen atoms belong to the two bridging H_2O molecules between two sodium sites, and the final oxygen donor is provided by a H_2O molecule acting as a terminal ligand. As expected for NaO_6 sites,[20] the geometry around sodium is very distorted and the Na−O distances average 2.372 Å. Interestingly, the $(NBu_4n)Na[Mo\{O_2CC(S)Ph_2\}_3]\cdot H_2O\cdot MeOH$ complex shows a very similar structure, with respect to the coordination not only about the transition metal but also about the central Na_2O_2 ring. In this case the terminal H_2O ligands coordinated to sodium ions in the $Na(\mu\text{-}H_2O)_2Na$ unit have been replaced by CH_3OH molecules.[17]

Solution of the structure of this complex revealed a partial oxidation of the thiolate groups, apparently to sulfinate, in a small fraction of the CoS_3O_3 sites. This presumably occurred during the crystallization process of the Co(III) complex under an open atmosphere. The oxidation involves only one out of the three thiolate functions in the coordination sphere of each Co atom and has no significant effect on the Co−S bonding distance. We have interpreted the partial oxidation and resultant structural disorder as 22% substitution of S by SO_2 in this ligand, but crystallographically this cannot be distinguished from a more complicated disorder involving alternative orientations of an SO group. Oxidation reactions of metal thiolate complexes leading to the formation of sulfinate complexes have been characterized, particularly in the case of nickel. The oxidation with oxygen is of general interest to the oxidative deactivation of metallocysteinato enzymes and to the oxidative metabolism of cysteine.[26] To our knowledge, the $\{Co(SC_6H_4COO)_3\}^{3-}$ unit provides the first example of a spontaneous aerial oxidation of a thiolate in a Co(III) complex.

$(NEt_4)_3Na_3[\{Co(SC_6H_4COO)_3\}_2]\cdot 6MeOH$ (4). The structure of this complex contains discrete $[Na_3\{Co(SC_6H_4COO)_3\}_2(MeOH)_6]^{3-}$ anions and $NEt_4{}^+$ cations (both ordered and disordered). All the metals and the disordered cation lie on crystallographic C_3 axes, while the ordered cation has crystallographic C_2 symmetry. This anion can be described as a pentanuclear Na_3Co_2 species consisting of two dinuclear [{Co^{III}-

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(18) Saadeh, S. H.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 8−15.

(19) Vittal, J. J.; Dean, P. A. W. *Inorg. Chem.* **1993**, *32*, 791−794.

(20) Brechin, E. K.; Gilby, L. M.; Gould, R. O.; Harris, S. G.; Parsons, S.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2657−2664.

(21) Ollis, J.; Das, M.; James, V. J.; Livingstone, S. E.; Nimgirawath, K. *Cryst. Struct. Commun.* **1976**, *5*, 679−682.

(22) Xu, Y. J.; Kang, B. S.; Chen, X. T.; Huang, L. R. *Acta Crystallogr., Sect. C* **1995**, *51*, 370−374.

(23) Hu, Y.; Weng, L.; Huang, L.; Chen, X.; Wu, D.; Kang, B. *Acta Crystallogr., Sect. C* **1991**, *47*, 2655−2656.

(24) Manivannan, V.; Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 769−771.

(25) Freyberg, D. P.; Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1979**, *11*, 3037−3043.

(26) Mirza, S. A.; Pressler, M. A.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1993**, *32*, 977−87.

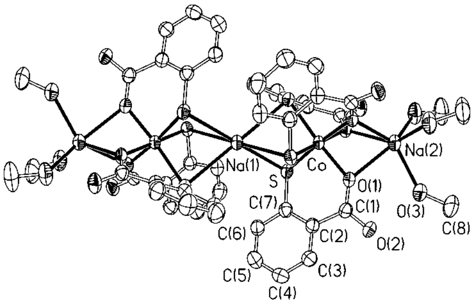

Figure 3. View of the pentanuclear anion assembly with S_6 symmetry in complex **4**.

$(S\cap O)_3\}Na(CH_3OH)_3]$ fragments linked to a central sodium ion, which is located on a crystallographic inversion center (in fact, a site of S_6 symmetry), Figure 3. Extending the concept of cobalt complexes acting as ligands for sodium centers, the anion can be regarded as consisting of two CoS_3O_3 metalloligands and three sodium ions, which play different roles in the connectivity of the structure. One sodium, Na(1), is responsible for linking the two CoS_3O_3 metalloligands together. Each metalloligand is also bound to a second sodium, Na(2), or its symmetry-related equivalent, which completes its coordination sphere with three methanol molecules and thus behaves as a terminal unit in the pentanuclear species. The geometry around Co(III) in the $\{Co^{III}(S\cap O)_3\}$ unit is an octahedron with three sulfur atoms and three oxygen atoms from three bidentate $^{-}SC_6H_4COO^{-}$ ligands. The behavior of the carboxylate groups as monodentate in the CoS_3O_3 site, the facial disposition of sulfur and oxygen atoms about the cobalt center, and the geometric parameters in the $\{Co^{III}(S\cap O)_3\}$ unit are very similar to those found in the other Co(III) complexes, **3** and **7**, as already mentioned.

The crystallographically independent Na(1) is bound to six sulfur atoms with six equal Na(1)−S bonding distances of 2.8172(7) Å in a distorted geometry (trigonally elongated octahedral). It appears to be the first structurally characterized example of a NaS_6 site. Species involving the interaction of sodium sites with S-donors are scarce. To date, the maximum number of sodium−sulfur contacts is three as reported for the NaS_3O_3 site in the complexes $[(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3]$, where R = Bu^t or Ph.[27] The sulfur atoms in the NaS_6 site of complex **4** derive from the $^{-}SC_6H_4COO^{-}$ ligands of two $\{Co^{III}(S\cap O)_3\}$ units, and the sodium ion, Na(1), is located between the S_3-triangular faces of two CoS_3O_3 octahedra.

The Na(2) ion and its symmetry-related equivalent are six-coordinate to oxygen atoms in an irregular environment. Three oxygen donors are derived from the carboxylate groups of the $^{-}SC_6H_4COO^{-}$ ligands. They constitute the vertexes of the O_3-triangular face, opposite the S_3 face, of the CoS_3O_3 octahedron. These oxygen atoms are μ_2-bridging between cobalt and sodium. The exocyclic oxygen atoms of the carboxylate groups are not involved in coordination. Three methanol molecules act as terminal ligands and complete coordination about Na(2).

Cobalt(III) Complex of the Methyl Ester of Thiosalicylic Acid: $[Co(SC_6H_4COOMe)_3]$ (7). This complex consists of mononuclear neutral molecules, Figure 4, where the thiolate sulfur and the carbonyl oxygen of three bidentate $^{-}SC_6H_4COOMe$ ester ligands coordinate to the only crystallographically independent cobalt. The three ligands are not crystallographically symmetry related, and thus the S_3O_3 octahedral coordination environment about cobalt is slightly distorted. Only the facial isomer is present in the unit cell. Main bond angles and distances deserve no special comment as they compare very well with the geometric parameters found for the $Co^{III}S_3O_3$ site in $[Na\{Co(SC_6H_4COO)_3(H_2O)_2\}]_2^{4-}$, $[Na_3\{Co(SC_6H_4COO)_3\}_2(MeOH)_6]^{3-}$, and closely related species, Table 2.

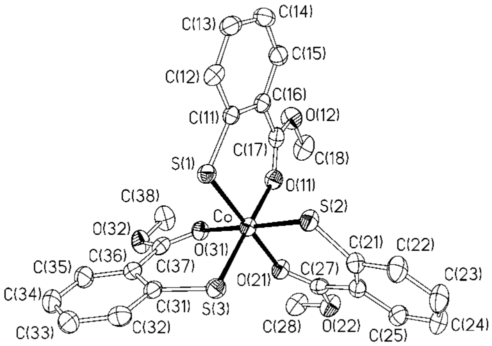

Figure 4. View of the molecule of complex **7**.

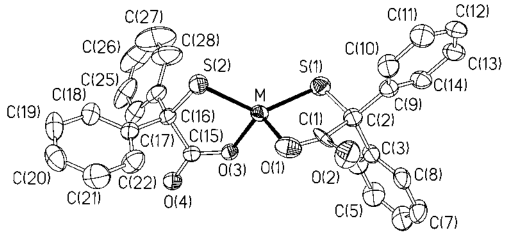

Figure 5. View of the molecule of complex **8** (M = Zn). Complex **9** (M = Co) is isostructural.

Zinc(II) and Cobalt(II) Complexes of 2,2-Diphenyl-2-mercaptoacetic Acid: $(NEt_4)_2[M\{Ph_2C(S)COO\}_2]$, M = Zn(II) (8) or Co(II) (9). The title Zn and Co complexes are isostructural in the solid phase. They consist of discrete $[M\{Ph_2C(S)COO\}_2]^{2-}$ anions and disordered NEt_4^+ cations. The detailed anion structure is provided in Figure 5, and dimensional data are given in Table 2. The M−S and M−O distances in the $[M\{Ph_2C(S)COO\}_2]^{2-}$ anion compare well with those found in related complexes with ZnS_2O_2,[28−33] CoS_2O_2,[4,34] and CoS_3O or $CoSO_3$[35] and even CoS_4[36,37] coordination environments. In the case of $[Zn\{Ph_2C(S)COO\}_2]^{2-}$, the average Zn−S and Zn−O distances are in very good agreement with those found in the previously described $(NEt_4)Na[Zn(SC_6H_4COO)_2]\cdot H_2O$ (**2**) complex (Table 2). Due to the geometrical restriction of the five-membered ring $\overline{C-O-M-S-C}$ (average internal angles S−M−O: 88.53° for M = Zn; 87.42° for M = Co), the tetrahedral coordination about the metal is severely distorted

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(27) Leverd, P. C.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans*. **1993**, 2251−2254.

(28) Potocnaák, I.; Jurco, M. D.; Petriícek, V.; Cernák, J. *Acta Crystallogr., Sect. C* **1994**, *50*, 1902−1904.

(29) Cavalca, L.; Gasparri, G. F.; Andreetti, G. D.; Domiano, P. *Acta Crystallogr.* **1967**, *22*, 90−98.

(30) Cernák, J.; Adzimová, I.; Gérard, F.; Hardy, A. M. *Acta Crystallogr., Sect. C* **1995**, *51*, 392−395.

(31) Smolander, K.; Ahlgrèn, M.; Melník, M.; Skorsepa, J.; Györyovà, K. *Acta Crystallogr., Sect. C* **1994**, *50*, 1900−1902.

(32) Steniner, M.; Grützmacher, H.; Zolnai, L.; Huttner, G. *J. Chem. Soc., Chem. Commun.* **1992**, 689−690.

(33) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* **1976**, 67−70.

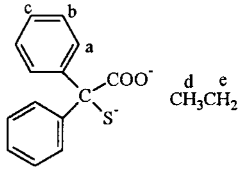
(34) Anderson, D. M.; Blake, A. J.; Fotheringham, J. D.; Stephenson, T. A.; Allan, J. R.; Veitch, P. M. *Acta Crystallogr., Sect. C* **1988**, *44*, 1305−1307.

(35) Brückner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Chem. Commun.* **1969**, 474.

(36) Dance, I. G. *J. Am. Chem. Soc.* **1979**, *101*, 6264−6273.

(37) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932−1934.

Table 3. Paramagnetic ^{1}H NMR Resonances of the Co(II) Complex **9** in CD_3CN at 298 K (20 mM Complex Concentration)



signal	δ (ppm)	assigned protons	no. of protons	T_1 (ms)	$\Delta\nu_{1/2}$ (Hz)	T_2 (ms)
a	65.8	*o*-Ph	4	0.5	1911	0.2
b	22.1	*m*-Ph	4	6.7	298	1.1
c	16.8	*p*-Ph	2	14.2	219	1.5
d	−8.7	$-CH_3$	12	10.8	511	0.6
e	−10.8	$-CH_2-$	8	6.0	648	0.5

with the angle S−M−S of about 130°. The average dihedral angle between the O(1)MS(1) and S(2)MO(3) planes is 103°.

The geometry about Co(II) in **9** compares well with that found in the only reported example of a thiolate complex containing a tetrahedral $Co^{II}S_2O_2$ core, $(NEt_4)_2[Co(mp)(Hmp)]_2$.[4] Not only are the Co−S and Co−O distances very close, but also both structures show a significant distortion from the ideal geometry about the metal center. Although the geometrical constraint of the five-membered ring is present in both complexes, the angles about cobalt(II) deviate more from those of a regular tetrahedron in the case of the $[Co(mp)(Hmp)]_2^{2-}$ anion, ranging from 86.4° to 141.6 °. This is probably due to the presence of two strong hydrogen bonds, which connect the two $[Co(mp)(Hmp)]^-$ fragments by means of the coordinated oxygen atoms.

Spectroscopic Properties in Solution: ^{1}H NMR Spectra of $(Et_4N)_2[Co(Ph_2C(S)COO)_2]$ (9). Paramagnetic ^{1}H NMR spectroscopy is a particularly useful technique for characterizing the electronic structure and coordination geometry of the metal ion in solution.[38] The isotropically shifted resonances, temperature dependence of the hyperfine-shifted proton resonances, and spin−lattice relaxation times are very sensitive to the electronic structure of the metal ion. The isotropic shift's proton resonances of paramagnetic systems may be of contact or pseudocontact origin or a combination of both. If the pseudocontact contribution is negligible, it can be assumed that the magnetic anisotropy is small.[39]

The 1D ^{1}H NMR spectrum of the Co(II) complex **9** in CD_3CN displays three well-resolved isotropically shifted signals (a−c) in the downfield region as well as two other signals (d and e) shifted upfield (Supporting Information). The proton NMR chemical shifts and T_1 values for complex **9** are reported in Table 3. Signals a−e display relatively short T_1 values from 0.5 ms (signal a) to 14.2 ms (signal c) and a broad line width (as measured at half-height) of ∼200−650 Hz, except for signal a (∼1900 Hz). These T_1 and $\Delta\nu_{1/2}$ values are characteristic of a four-coordinated Co(II) complex ($S = 3/2$).[40] Signals a and b integrate four protons each, whereas signal c integrates two protons. This together with the short T_1 values and the large chemical shifts of these signals gives evidence that they correspond to the phenyl protons. The other two signals (d and e), which also exhibit short T_1 values, integrate twelve and eight protons, respectively, and thus they can be assigned to the protons of the ethyl groups corresponding to the NEt_4^+ counterion (see Table 3).

The *ortho* and *meta* phenyl protons can be distinguished on the basis of their ^{1}H longitudinal relaxation times. In this sense, the T_1 values can be related to the M−H distance through the Solomon equation,[41] $T_1^{-1} \propto f(r^{-6})$. Thus, signal a (65.8 ppm) is assigned to the *ortho* phenyl protons, which are nearest to the cobalt(II) on the basis of its extremely short T_1 value. The specific assignment of the phenyl proton signals a and b for complex **9** is shown in Table 3. The large downfield paramagnetically shifted signal of the *ortho* phenyl protons can be interpreted as being due to a spin density delocalization on the d orbitals, as described elsewhere.[42]

The existence of a dipolar connectivity between signals b and c as well as d and e (Figure 6) confirms their vicinal origin and thus the assignment given in Table 3. In addition, signal a is dipolarly connected with signals b and c (data not shown), which present a NOESY cross-peak between them, as mentioned above. Despite extremely diverse acquisition and processing parameters, COSY cross-peaks were not observed.

Variable-temperature ^{1}H NMR spectra for complex **9** were registered from 240 to 350 K. In Figure 7, the measured isotropic shifts of the protons are plotted versus T^{-1} and we can observe a linear correlation. The usual procedure for verifying a non-T^{-1}-dependence of the chemical shifts is to extrapolate the plot to infinite temperature. Significant deviations from the zero extrapolation mean that a T^{-2} dependence can be present and there is possibly an important pseudocontact contribution to the isotropic shifts.[38] For **9**, the paramagnetically shifted proton signals are temperature dependent and only signal a shows an important deviation from the zero extrapolation (−24 ppm). These results indicate some dipolar contribution to the isotropic shifts of the *ortho* phenyl protons. As seen in Figure 7, the Co(II) complex **9** displays intercepts practically in the diamagnetic region (signals b−e), indicating that the isotropic shifts are essentially contact in origin as expected for tetracoordinated d^7 Co(II) complexes ($S = 3/2$) with an $^4A_2$ ground state. The magnetic anisotropy in these systems is insignificant in this temperature range. For this reason we can conclude that the observed isotropic shifts are due to contact contribution.[1b] Nonetheless, in the case of the *ortho* phenyl proton signals, which are the closest to the cobalt ion, some pseudocontact contributions to the isotropic shifts are detected as described above. Thus, the presence of zero-field splitting produces a dipolar contribution to the isotropic shift. The paramagnetic NMR studies are clearly consistent with the crystallographic studies previously described and show that complex **9** retains in solution the same geometry as that in the solid state.

On the other hand, the ^{1}H NMR spectrum isotropic shifts of complex **9** are concentration dependent. Moreover, the proton signals d and e, which correspond to the NEt_4^+ counterion, change in fast exchange conditions. This effect has been interpreted as being due to the ionic interaction between the anionic Co(II) complex and the NEt_4^+ counterion. In fact, signals d and e move upfield ranging from −4 to −15 ppm for concentrations of the cobalt complex in the range 3−62 mM. The changes in shifts can be fitted by the following equilibria: $M^{2-} + I^+ \leftrightarrow MI^-$ and $MI^- + I^+ \leftrightarrow MI_2$ ($M^{2-} = [Co\{Ph_2C(S)COO\}_2]^{2-}$, $I^+ = NEt_4^+$). The values of the ion pairing association constants obtained were $\log K_1 = 2.2$ and $\log K_2 =$

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(38) Bertini, I.; Luchinat C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin/Cummings: Boston, 1986.

(39) La Mar, G. N., Horrocks, W. D., Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(40) Banci, L.; Bertini, I.; Luchinat, C.; Donaire, A.; Martínez, M. J.; Moratal, J. M. *Comments Inorg. Chem.* **1990**, *9*, 245−261.

(41) Solomon, I. *Phys. Rev.* **1955**, *99*, 559−565.

(42) Bertini, I.; Luchinat, C. NMR of paramagnetic substances. In *Coordination Chemistry Reviews*; Lever, A. B. P., Ed.; Elsevier: Amsterdam, 1996; Vol. 150.

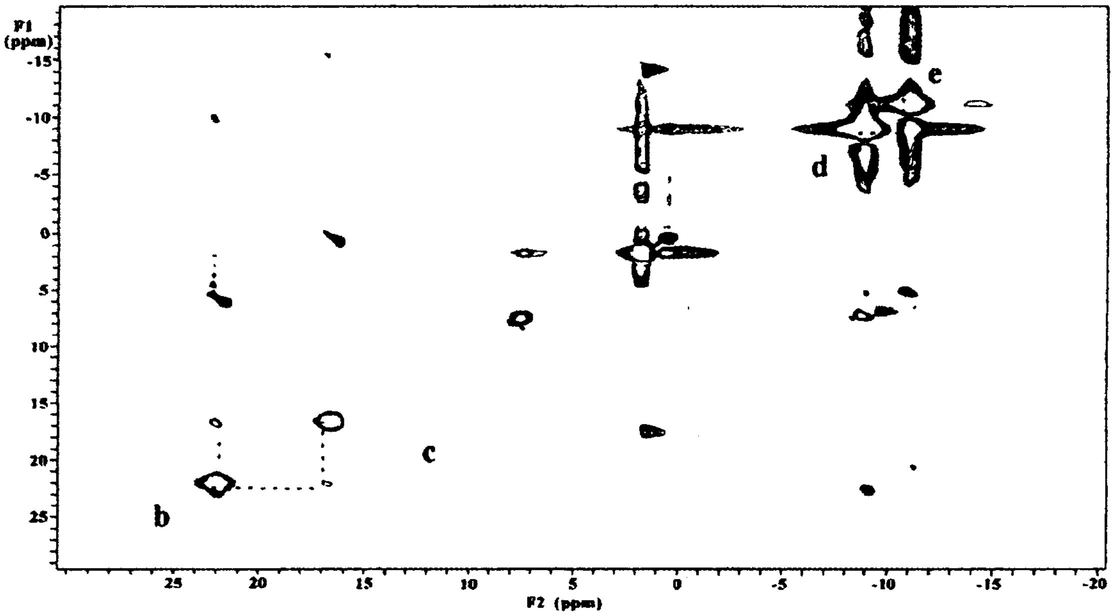

Figure 6. Portions of 400 MHz NOESY maps of cobalt(II) complex **9** in CD_3CN solvent (298 K, 20 mM complex concentration). Conditions are given in the text.

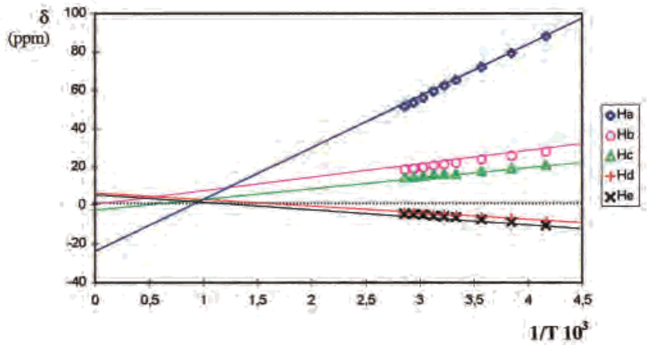

Figure 7. Temperature dependence of the ^1H NMR hyperfine-shifted resonances of Co(II) complex **9** (CD_3CN solvent, 10 mM complex concentration). The range of temperature is ca. 240−350 K. Protons are labeled according to Table 12.

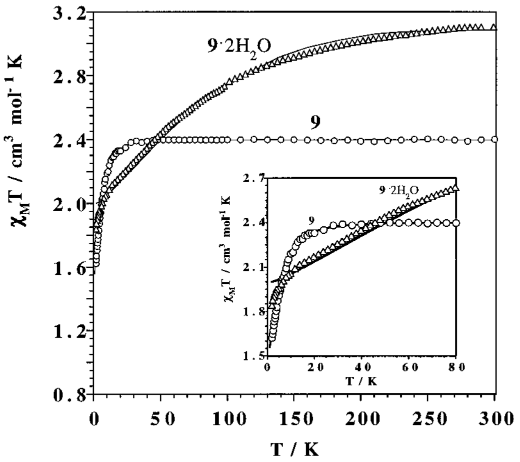

Figure 8. Thermal dependence of $\chi_M T$ for **9** and **9**·$2H_2O$. The solid lines are the calculated curves (see the text).

1.7 (300 K), respectively. Earlier studies on ion pair formation involving a paramagnetic anion and a diamagnetic cation have reported a similar behavior.[43,44]

Magnetic Susceptibility Measurements of $(Et_4N)_2$[Co-$(Ph_2C(S)COO)_2$] (9). The magnetic properties of complex **9** and its dihydrated derivative (**9**·$2H_2O$) under the form of $\chi_M T$ versus T (χ_M being the molar magnetic susceptibility) are shown in Figure 8. The inset shows the low-temperature region for both compounds. In the case of **9** the $\chi_M T$ values remain nearly constant in a wide range of temperatures and smoothly decrease at low temperatures. In principle, the slight decrease of $\chi_M T$ at low temperature could be attributed to intermolecular interactions and/or zero-field splitting (zfs) effects. The presence of a ligand-field component of symmetry lower than cubic can cause the magnetic moment to vary with T, as the spin degeneracy of the $^4A_2$ ground state is then lifted. The fact that **9** is well isolated magnetically indicates that, most likely, the zero-field splitting is the responsible factor for the slight decrease of $\chi_M T$. For a d^7 ion in a tetrahedral environment, the first excited state is $^4T_2$ arising from the ^4F free-ion ground state. Under a tetragonal distortion, this state is split into an orbital singlet, $^4B_2$, and an orbital doublet, ^4E, at energies $\Delta_{\|}$ and $\Delta_{\perp}$, respectively. The actual symmetry of **9** is still lower, C_{2v} (idealized symmetry). For this point group, the orbital doublet ^4E is split into two orbital singlets, $^4B_1$ and $^4B_2$, at energies Δ_x and Δ_y, respectively. However, due to the close equivalence of the x and y axes in four-coordinated CoL_2^{2-} entity, both singlets remain basically degenerated, that is, $\Delta_x = \Delta_y = \Delta_{\perp}$. So, the tetragonal symmetry (Scheme 2) applies for this monomeric complex. The quartet spin ground state, $^4A_2$, is removed by the combined action of the spin−orbit interaction and the tetragonal crystal field, leading to two Kramers doublets (zero-field splitting). The $^4T_2$ splitting is related to the zero-field splitting of the ground state through eq 1,[45] where λ is the spin−orbit coupling parameter and the meaning of the remaining terms is clear from Scheme 2.

$$D = 8\lambda^2\left(\frac{1}{\Delta_{\perp}} - \frac{1}{\Delta_{\|}}\right) \qquad (1)$$

Formally, this behavior can be treated as an $S = 3/2$ spin state under the action of the spin Hamiltonian $H = D[S_z^2 -$

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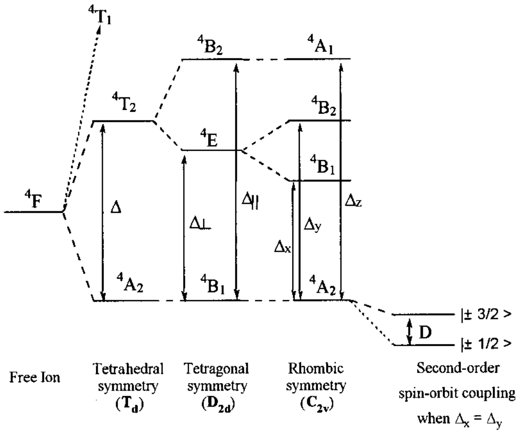
[43] Bertini, I.; Luchinat, C.; Borghi, E. *Inorg. Chem.* **1981**, *20*, 303−306.

[44] Lim, Y.; Drago, R. S. *J. Am. Chem. Soc.* **1972**, *94*, 84−90.

[45] Figgis, B. N. *Trans. Faraday Soc.* **1960**, *56*, 1553−1560.

[46] Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

Scheme 2



$^1/_3S(S + 1)] + g_\parallel\beta H_zS_z + g_\perp\beta(H_xS_x + H_yS_y)$, where DS_z^2 represents the splitting into two Kramers doublets in the absence of a magnetic field. In the present notation, positive D values stabilize the ±1/2 state. The expression of the magnetic susceptibility in eqs 2 and 3 is easily derived from the above-mentioned Hamiltonian,[46] the parameters therein involved having their usual meaning.

$$\chi_\parallel = \frac{N\beta^2}{4kT}g_\parallel^2F_{D\parallel} \tag{2}$$

$$\chi_\perp = \frac{N\beta^2}{4kT}g_\perp^{\ 2}F_{D\perp} \tag{3}$$

$$F_{D\parallel} = \frac{1 + 9\exp\left(-\frac{D}{kT}\right)}{1 + \exp\left(-\frac{D}{kT}\right)} \tag{4}$$

$$F_{D\perp} = \frac{4 + 6\frac{kT}{D}\left[1 - \exp\left(-\frac{D}{kT}\right)\right]}{1 + \exp\left(-\frac{D}{kT}\right)} \tag{5}$$

Least-squares fitting of the experimental data through this expression leads to $D = 10.8(2)\ \text{cm}^{-1}$, $g_\parallel = 2.20(1)$, and $g_\perp = 2.29(1)$. A good fit can also be obtained using $g_\parallel = g_\perp = g_{av} = 2.27(1)$. It should be noted that the quality of the fit is very good even at very low temperatures without the inclusion of intermolecular magnetic interactions.

Values of $|D|$ of about ca. 10 cm^{-1} have already been reported for other tetrahedrally distorted cobalt(II) complexes.[47] This relatively large value of D can be understood keeping in mind the relatively large value of the spin−orbit parameter of Co(II) (λ = ca. −180 cm^{-1} for a single ion), the small ligand-field strength for tetrahedral complexes (Δ = ca. 4000 cm^{-1}), and the relatively large splitting of the $^4T_2$ term due to the low symmetry (C_{2v}) and the substantial difference between the two types of donor atoms (O and S). In fact, using a ligand-field strength Δ = ca. 4000 cm^{-1} and a λ value of 150 cm^{-1} (after its reduction by covalency effects, k = ca. 0.85), a $^4T_2$ splitting ($\Delta_\parallel - \Delta_\perp$) of ca. 1500 cm^{-1} can be easily estimated through eq 1.

As mentioned above, compound **9** takes water molecules changing its color from deep blue to pale pink. This hydration dramatically changes its magnetic properties, Figure 8, which agree with the formula **9**·$2H_2O$ as the χ_MT curve is characteristic of an octahedral Co(II) complex. The greater χ_MT value at room temperature of **9**·$2H_2O$ with respect to that of **9** can be attributed to the orbital contribution of the orbitally degenerate ground state, $^4T_1$, of Co(II) in an octahedral environment (turning Scheme 2 upside down). Attempts to theoretically reproduce its magnetic behavior using the susceptibility equations proposed for Co(II) complexes in a strict octahedral symmetry failed, indicating that an important distortion is present.

Magnetic data of **9**·$2H_2O$ can be interpreted quite satisfactorily assuming an important axial distortion about the Co(II) ions. For that, we used the matrixes of $^4T_1$, under the combined action of the spin−orbit coupling and an axial ligand-field component, which were reported by Figgis et al.[48] The relevant parameters involved are A (ligand-field strength, $1 \le A \le 1.5$, which takes into account the degree of mixing of the two $^4T_1$ states arising from the ground-state ^4F and excited ^4P terms of the d^7 free ion), k (orbital reduction), λ (spin−orbit coupling), and δ (splitting of the $^4T_1$ term by the axial ligand-field component). A reasonable fit was obtained for $A = 1.4$, $k = 1$, $\lambda = -160\ \text{cm}^{-1}$, and $\delta = 800\ \text{cm}^{-1}$.

Although the determination of these parameters is not unambiguous (specially δ), the values that we have obtained are reasonable, and they can describe by themselves the magnetic behavior of **9**·$2H_2O$ above 10 K without intermolecular magnetic interactions. However, the magnetic data at lower temperatures present significant deviations from the theoretical curve. The experimental χ_MT values, which decrease more quickly, indicate that small intermolecular magnetic interactions occur, possibly due to hydrogen bonds between the coordinated water molecules.[49]

Summary and Conclusions

The use of a redox-active and thus a redox-noninnocent ligand has been demonstrated as a good strategy to overcome the ease of oxidation of species containing a tetrahedral $Co^{II}S_2O_2$ core. Thus, the 2,2-diphenyl-2-mercaptoacetic acid ligand has allowed not only the preparation but also the full structural characterization in the solid phase and in solution of the first mononuclear Co(II) complex, $(NEt_4)_2[Co\{Ph_2C(S)COO\}_2]$, with a tetrahedral $Co^{II}S_2O_2$ core. In our opinion, the ability of this ligand to undergo an oxidative decomposition gives rise to a reductive atmosphere, which allows formation of an otherwise highly oxidizable species. Once formed, the Co(II) complex is stable in the solid phase as well as in solution under an open atmosphere. The zinc complex $(NEt_4)_2[Zn\{Ph_2C(S)COO\}_2]$ is shown to be isostructural, both with distorted tetrahedral coordination about the metal center. Studies on the temperature dependence of magnetic susceptibility in the range 2.0−300 K have allowed the magnetic characterization of the $(NEt_4)_2[Co\{Ph_2C(S)COO\}_2]$ complex as well as the determination of its corresponding electronic states. This complex adds H_2O reversibly under ambient conditions. Magnetic measurements of the hydrated form in the same temperature range give evidence of an octahedral coordination about the cobalt(II) center. In addition, according to electronic UV−vis data and paramagnetic 1D and 2D ^1H NMR experiments, the $[Co\{Ph_2C(S)COO\}_2]^{2-}$ complex preserves its tetrahedral geometry in solution.

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(47) Nelson, D.; Haar, L. W. *Inorg. Chem.* **1993**, *32*, 182−191 and references therein.

(48) Figgis, B. N.; Gerloch, M.; Lewis, J.; Mabbs, F. E.; Webb, G. A. *J. Chem. Soc. A* **1968**, 2086−2094.

(49) De Munno, G.; Viterbo, D.; Caneshi, A.; Lloret, F.; Julve, M. *Inorg. Chem.* **1994**, *33*, 1585−6.

The detailed characterization of the $Co^{II}S_2O_2$ core in the $[Co\{Ph_2C(S)COO\}_2]^{2-}$ complex has a potential bioinorganic interest as a model for tetrahedral MS_2O_2 active sites in Co(II)-substituted metalloproteins. One such site is present in the recently reported structure of *Desulfovibrio fructosovorans* hydrogenase, which features an M_2(*S*-Cys)$_2$ core composed of one Ni center and one Fe center. The latter completes coordination with two oxygen atoms of two water molecules (pdb 1frf).

Other chelating ligands, such as thiosalicylic acid and the corresponding methyl ester, under strict anaerobic conditions, have not allowed stabilization of Co(II) in a sulfur−oxygen coordination environment. Instead, a series of Zn(II) and Co(III) complexes has been prepared and structurally characterized. A particular interest of the complexes with thiosalicylic acid is that the framework of the heterobimetallic zinc−sodium and cobalt−sodium complexes obtained is mainly determined by the involvement of sodium ions as a structural element.

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Supporting Information Available: Proton and ^{13}C NMR data for complexes **1**−**5**, **7**, and **8** (Table S1), main infrared absorption bands corresponding to vibrations of the COO^- and C═O groups in complexes **1**−**5** and **7**−**9** (Table S2), solution absorption spectral data and ligand field spectral parameters for octahedral $Co^{III}S_3O_3$ (**3**, **4**, **7**) and tetrahedral $Co^{II}S_2O_2$ (**9**) complexes (Table S3), the 400 MHz ^1H NMR spectrum of cobalt(II) complex **9** in CD_3CN at 300 K (10 mM complex concentration) (Figure S1), and six crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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