

# A New Oxygen-Sulfur Anion: Preparation and Structure of Potassium $\mu$ -(Thiosulfito-S,S')-decacyanodicobaltate(III)

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**Abstract:** Exposure to air of a saturated solution of  $(\text{CN})_5\text{CoS}_2\text{Co}(\text{CN})_5^{6-}$  in a mixture of ethanol and water at  $-15^\circ\text{C}$  leads to the slow formation of the binuclear anion  $(\text{CN})_5\text{CoSSO}_2\text{Co}(\text{CN})_5^{6-}$ , in which the bridging thiosulfito group is coordinated through the two sulfur atoms to the two cobalt atoms. This complex can be isolated in crystalline form as the solvated potassium salt  $\text{K}_6[\text{Co}_2\text{SSO}_2(\text{CN})_{10}] \cdot (\text{H}_2\text{O})_{\sim 6.1}(\text{C}_2\text{H}_5\text{OH})_{\sim 0.4}$ . The crystal structure of this salt has been determined by single-crystal X-ray diffraction methods and refined to an  $R$  value of 0.052 for 3250 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The space group is  $C2/c$ ; the cell dimensions are  $a = 36.860(15)$  Å,  $b = 9.241(2)$  Å,  $c = 20.772(12)$  Å, and  $\beta = 124.10(3)^\circ$ . The  $\text{CoSSCo}$  unit is planar, with distances  $\text{Co-S}(\text{sulfito}) = 2.255(2)$  Å,  $\text{Co-S}(\text{thio}) = 2.297(2)$  Å,  $\text{S-S} = 2.064(3)$  Å; the average  $\text{S-O}$  distance is  $1.468(4)$  Å. The  $\text{Co}(\text{CN})_5$  groups have normal geometry with only small indications of trans influences, suggesting that both sulfur atoms can compete successfully with CN for  $\pi$ -bonding density.

The synthesis of the binuclear  $\mu$ -dithio-cyanocobalt ion  $(\text{CN})_5\text{CoS}_2\text{Co}(\text{CN})_5^{6-}$  has been reported;<sup>2</sup> in the synthesis, pentacyanocobaltate(II) is used to reduce elemental sulfur. The binuclear anion is isolable as the potassium salt in the form of a brown powder and has been characterized spectroscopically as containing the disulfide-bridging ligand in the same staggered conformation as is found in the analogous peroxy complex.<sup>3</sup> Binuclear ions containing only disulfide as a bridging ligand are rare; the only published structure we are aware of is that of the ion  $(\text{NH}_3)_5\text{RuSSRu}(\text{NH}_3)_5^{4+}$ .<sup>4</sup> Because of this rarity we were interested in determining the structure of the cobalt compound and comparing it with that of the peroxy complex. However, our attempts to grow diffraction quality crystals of the potassium salt of the  $\mu$ -disulfide complex have led instead to the formation of a new complex containing the bridging ligand thiosulfite ( $\text{SSO}_2^{2-}$ ), an ion that has not been identified previously. An X-ray crystal structure analysis has characterized the new compound as  $\text{K}_6[(\text{CN})_5\text{CoSSO}_2\text{Co}(\text{CN})_5] \cdot (\text{H}_2\text{O})_{\sim 6.1}(\text{C}_2\text{H}_5\text{OH})_{\sim 0.4}$ . Our search for information about the thiosulfite ion turned up only occasional mention in the ancient literature of thiosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_2$ , as an intermediate or a component of a mixture. Schenk and Ludwig<sup>5</sup> claimed to have isolated the acid at  $-70^\circ\text{C}$  as a white powder that decomposes to  $\text{SO}_2$  and  $\text{H}_2\text{S}$  on warming.

## Experimental Section

A sample of the potassium salt of  $\text{Co}_2\text{S}_2(\text{CN})_{10}^{6-}$  was prepared by the method of Siebert and Thym,<sup>2</sup> using cobaltous acetate and KCN as starting materials. The dark orange-brown product is extremely soluble in water and tends to form a dark brown, almost black oil when precipitated from aqueous solution by using ethanol. In an attempt to grow crystals, an equal volume of cold ethanol was added to a concentrated aqueous solution of the brown powder at  $0^\circ\text{C}$ , and the mixture was cooled to  $-15^\circ\text{C}$ , resulting in overnight reprecipitation of the brown powder with poor crystal formation. The crystallization vessel containing the brown precipitate and light brown transparent mother liquor was maintained at  $-15^\circ\text{C}$  exposed to the air for approximately 8 weeks, after which time well-formed orange crystals were noted growing amid the brown precipitate. These prismatic crystals are fairly intensely colored but noticeably lighter than the dithio complex. The solid products were collected by suction filtration and washed with ethanol and ether. The orange crystals were separated in pure form by discriminatory crystal picking under a microscope and were visibly free from extraneous impurities. F.R.F. has often tried to repeat this synthesis but has never been able to isolate the same compound. The electronic absorption spectrum of the orange material shows maxima at 258 and 310 nm and a shoulder

Table I. Crystal Data for  $\text{K}_6[\text{Co}_2\text{SSO}_2(\text{CN})_{10}] \cdot (\text{H}_2\text{O})_{\sim 6.1}(\text{C}_2\text{H}_5\text{OH})_{\sim 0.4}$

fw	837.11	$V$ , Å <sup>3</sup>	5859 (7)
space group	$C2/c$	$\rho(\text{exptl})$ , g/cm <sup>3</sup>	1.83 (1)
$Z$	8		
$a$ , Å	36.860 (15)	$\rho(\text{calcd})$ , g/cm <sup>3</sup>	1.897 (5)
$b$ , Å	9.241 (2)	$\lambda(\text{Mo K}\alpha)$ , Å	0.710 69
$c$ , Å	20.772 (12)	$\mu$ , cm <sup>-1</sup>	21.6
$\beta$ , deg	124.10 (3)		

at 360 nm. Due to the microscopic quantities of material available, molar extinction coefficients for these bands were not obtainable; however, they appear to be greater than  $10^3$ . The UV-vis spectrum of the orange crystals is clearly different from that of the dithio complex.<sup>2</sup>

X-ray diffraction photographs established the crystals as monoclinic with a centered cell; systematic absences  $hkl$  with  $h+k$  odd and  $h0l$  with  $l$  odd are consistent with space groups  $Cc$  and  $C2/c$ . Visual examination of the intensity distribution on upper-layer Weissenberg films led to the judgment that the centric space group  $C2/c$  is more likely correct, as did more formal distributions calculated later. The density measured by flotation in  $\text{CCl}_4\text{-CHBr}_3$  indicated a unit-cell mass consistent with eight formula units of the expected  $\mu$ -dithio complex plus another 300 or so atomic mass units.

A crystal of approximate dimensions  $0.45 \times 0.30 \times 0.26$  mm was mounted with its long dimension ( $b$ ) coincident with the  $\phi$  axis of a General Electric XRD quarter-circle diffractometer automated by Daxex and equipped with a proportional counter and graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71069$  Å). Lattice constants were obtained from a least-squares fit to  $2\theta$  values of 12 high-angle reflections. Integrated intensities were obtained by  $\theta$ - $2\theta$  scans of all unique reflections between  $2\theta = 4^\circ$  and  $2\theta = 50^\circ$ , with scans including both the  $\alpha_1$  and  $\alpha_2$  components of the peaks. Scan widths varied linearly with  $2\theta$ , with a zero-angle width of  $1.84^\circ$  and an increase in width of  $0.0123^\circ/\text{degree}$  in  $2\theta$ . The scan speed was  $2^\circ/\text{min}$ , with backgrounds counted for 20 s at each extreme of the scan; all data with  $2\theta$  between  $40^\circ$  and  $50^\circ$  were then recollected at a scan speed of  $1^\circ/\text{min}$  with 40-s background measurements. In all, 5084 independent reflections were measured, of which 4604 had positive net intensities. Five reflections widely distributed in reciprocal space were remeasured periodically during data collection; the  $F$  values of these standards declined fairly uniformly by about 9%. Linear decay corrections were applied to the data by using the check reflections as a guide.

Absorption corrections were made by the method of Gaussian quadrature,<sup>6</sup> with the integration being performed over a grid of  $8 \times 8 \times 8$  points; the transmission coefficients ranged from 0.59 to 0.66. After Lorentz and polarization corrections were applied, the data were placed on an approximately absolute scale by the method of Wilson.<sup>7</sup> Observational variances  $\sigma^2(F_o^2)$  were assigned on the basis of counting statistics plus a term  $(0.02S)^2$ , where  $S$  is the scan count, to allow for instrumental variations.<sup>8</sup> Crystal data are given in Table I.

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Table II. Final Parameters<sup>a</sup> for  $K_6[(CN)_5CoSSO_2Co(CN)_5](H_2O)_{\sim 6.1}(C_2H_5OH)_{\sim 0.4}$ 

atom	x	y	z	pop. <sup>b</sup>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co(1)	1506 (0.3)	2394 (0.9)	5241 (0.5)		31 (0.4)	30 (0.5)	27 (0.4)	-1 (0.4)	18 (0.4)	-1 (0.4)
Co(2)	951 (0.3)	1501 (0.9)	7231 (0.5)		27 (0.4)	33 (0.5)	25 (0.4)	0 (0.4)	15 (0.4)	-1 (0.4)
S(1)	1329 (0.6)	2661 (2)	6133 (1)		54 (1)	34 (1)	40 (1)	-6 (1)	35 (1)	-5 (1)
S(2)	1100 (0.5)	824 (2)	6360 (1)		32 (1)	31 (1)	35 (1)	2 (1)	24 (1)	0 (1)
O(1)	708 (2)	299 (5)	5634 (3)		51 (3)	59 (3)	41 (3)	-14 (3)	32 (3)	-18 (3)
O(2)	1445 (2)	-283 (5)	6681 (3)		61 (3)	52 (3)	75 (4)	20 (3)	52 (3)	19 (3)
N(1)	1778 (2)	2620 (8)	4121 (4)		88 (5)	90 (5)	65 (5)	-17 (5)	63 (4)	-9 (4)
N(2)	2433 (2)	3243 (7)	6519 (4)		36 (3)	58 (4)	53 (4)	-4 (3)	18 (3)	-3 (3)
N(3)	1803 (2)	-724 (7)	5569 (4)		53 (4)	50 (4)	76 (5)	5 (3)	33 (4)	-4 (4)
N(4)	581 (2)	1509 (7)	3937 (3)		46 (4)	65 (4)	34 (3)	-6 (3)	19 (3)	-9 (3)
N(5)	1255 (2)	5550 (7)	4910 (6)		79 (5)	41 (4)	57 (4)	13 (4)	29 (4)	6 (3)
N(6)	683 (2)	2201 (7)	8337 (4)		82 (5)	60 (4)	53 (4)	-14 (4)	52 (4)	-18 (3)
N(7)	1914 (2)	1116 (9)	8505 (5)		44 (4)	104 (7)	78 (6)	12 (4)	3 (4)	-9 (5)
N(8)	724 (2)	-1626 (6)	7303 (3)		55 (4)	44 (4)	45 (4)	0 (3)	31 (3)	1 (3)
N(9)	-3 (2)	1900 (8)	5933 (4)		32 (3)	84 (5)	49 (4)	5 (3)	19 (3)	-11 (4)
N(10)	1127 (2)	4711 (7)	7306 (4)		70 (4)	48 (4)	61 (4)	-5 (3)	49 (4)	-7 (3)
K(1)	0	123 (3)	1/4	4	34 (1)	58 (2)	37 (1)	0	14 (1)	0
K(2)	900 (0.5)	1745 (2)	9878 (1)		34 (1)	53 (1)	49 (1)	-3 (1)	23 (1)	10 (1)
K(3)	2291 (0.6)	667 (3)	7399 (1)		51 (1)	108 (2)	91 (2)	2 (1)	30 (1)	41 (1)
K(4)	4286 (0.7)	723 (2)	6911 (1)		77 (1)	66 (1)	65 (1)	3 (1)	47 (1)	8 (1)
K(5)	-52 (0.7)	1619 (3)	4444 (1)		67 (1)	137 (2)	59 (1)	4 (1)	36 (1)	-10 (1)
K(6)	3344 (0.5)	2427 (2)	7338 (1)		47 (1)	61 (1)	56 (1)	-4 (1)	33 (1)	-12 (1)
K(7)	2468 (2)	359 (6)	4899 (3)	4	61 (3)	115 (4)	71 (3)	1 (3)	11 (2)	-3 (3)
W(1)	4924 (2)	51 (7)	1647 (4)		74 (4)	87 (5)	81 (4)	-12 (4)	46 (4)	12 (4)
W(2)	755 (3)	3521 (9)	895 (4)		139 (7)	133 (7)	97 (6)	-29 (6)	81 (5)	-40 (5)
W(3)	1890 (2)	3231 (8)	1566 (4)		112 (6)	121 (6)	66 (5)	-35 (5)	26 (4)	11 (4)
W(4)	315 (3)	4220 (10)	4835 (5)		121 (6)	166 (8)	127 (7)	11 (6)	88 (6)	-10 (6)

atom	x	y	z	pop. <sup>b</sup>	$B, \text{Å}^2$	atom	x	y	z	pop. <sup>b</sup>	$B, \text{Å}^2$
W(5A)	2863 (5)	479 (16)	2085 (9)	3.8 (6)	6.1 (3)	C(6)	803 (2)	1945 (7)	7947 (4)		3.1 (1)
W(5B)	2820 (8)	419 (26)	1624 (14)	2.7 (3)	7.5 (5)	C(7)	1546 (2)	1245 (8)	8033 (4)		3.9 (1)
W(5C)	2783 (10)	1190 (31)	2078 (18)	1.9 (5)	6.1 (6)	C(8)	824 (2)	-460 (7)	7282 (4)		2.7 (1)
W(6)	7210	2090	5200	1.2	5.0	C(9)	355 (2)	1785 (7)	6406 (4)		2.6 (1)
W(7)	2546 (5)	7 (18)	5295 (9)	4	8.6 (5)	C(10)	1061 (2)	3474 (7)	7237 (4)		2.7 (1)
W(8)	2012 (5)	2963 (16)	9801 (8)	3.6	7.2 (4)	Et(O1)	6540	800	4000	1.6	7.0
C(1)	1667 (2)	2479 (8)	4531 (4)		3.2 (1)	Et(C1)	6850	1720	4520	1.6	6.0
C(2)	2086 (2)	2943 (7)	6042 (4)		2.6 (1)	Et(C2)	7210	1750	5360	1.6	7.0
C(3)	1683 (2)	453 (7)	5445 (4)		3.0 (1)	Et(O2)	7200	1490	5840	1.6	7.0
C(4)	929 (2)	1824 (7)	4436 (4)		2.8 (1)	Et(C3)	7180	1970	5170	1.6	6.0
C(5)	1346 (2)	4369 (7)	5037 (4)		2.9 (1)	Et(C4)	6900	1400	4350	1.6	7.0

<sup>a</sup> Coordinates have been multiplied by  $10^4$  and  $U_{ij}$  values by  $10^3$ . The anisotropic temperature factor is of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{23}klb^*c^*)]$ . <sup>b</sup> The number of atoms in a unit cell. Where no entry is given, the number is 8, the general multiplicity of  $C2/c$ .

A Patterson map was prepared, but we were unable to find a satisfactory solution in space group  $C2/c$ . We then resorted to space group  $Cc$  and deduced a model, with two formula units in the asymmetric unit, containing all heavy (Co, S, and K) atoms except for two potassium ions. The remaining atoms, including the unexpected sulfite oxygen atoms, were soon found, and the complete model was refined by least squares to an  $R$  of 0.117 and a goodness-of-fit (GOF) of 5.2. This model, however, had some disconcerting features, including Co-C distances which varied over a range that taxed credulity, some Co-C-N angles which differed from linearity by almost  $40^\circ$ , and totally unreasonable temperature factors for some of the ligand atoms. An approximate center of symmetry between most pairs of atoms was then noted, and although two of the potassium ions and most of the solvent structure (which had been identified as water molecules) did not conform to the centrosymmetric model, we recast the structure in space group  $C2/c$ . This model, which yielded an initial  $R$  of 0.22, contained only five and half potassium ions per asymmetric unit, since K(1) lay on a twofold axis; a subsequent Fourier synthesis suggested an additional ion, K(7), in a half-populated general position. Refinement of this model led to reasonable geometry and temperature factors.

A large number of difference maps calculated at various refinement stages indicated four discrete water molecules, in ordered sites, per asymmetric unit and showed residual electron densities in three other regions. One of these regions, close to K(7), was interpreted as a half-populated site for a water molecule, W(7), present whenever K(7) is absent. A second region suggested three partially occupied sites, W(5a, 5b, 5c); the populations of these three sites, refined by least squares, summed satisfactorily close—1.05 (10)—to a full water molecule (see Table II). The third region was more complicated, showing several poorly resolved peaks separated by as little as 0.6 Å. It was eventually

fit with two ethanol molecules with populations 0.2 each, a water molecule with population 0.45, and another water molecule with population 0.15.

In the final least-squares cycles, 300 parameters were adjusted in two matrices, one containing coordinates of all atoms except those of the partial ethanol groups and the 0.15-populated water molecule, and the second containing anisotropic  $U$ 's for Co, K, S, N, and the O atoms of the anion and of the ordered water molecules, isotropic  $B$ 's for the remaining atoms whose coordinates were adjusted, and a scale factor. The hydrogen atoms of the various solvent groups were ignored. Refinement was terminated when all shifts were less than 0.5 esd and all shifts for the potassium ions and the atoms of the binuclear cation were less than 0.2 esd.

The final  $R$  is 0.076 for the 4604 reflections with  $F^2 > 0$  and 0.052 for the 3250 reflections with  $F_o^2 \geq 3\sigma(F_o^2)$ ; the goodness-of-fit  $([\sum w(F_o^2 - F_c^2)^2 / (5084 - 300)]^{1/2})$  is 1.91 for all 5084 data. A final difference map showed excursions up to  $\pm 0.65 \text{ e} \cdot \text{Å}^{-3}$  in the solvent regions and up to  $\pm 0.8 \text{ e} \cdot \text{Å}^{-3}$  elsewhere.

Machine calculations were performed by using an IBM 370/158 and a DEC VAX 11/780 computer with programs in the CRYM system, as well as ORTEP.<sup>9</sup> The quantity minimized in the least-squares calculations was  $\sum w(F_o^2 - F_c^2)^2$ , with  $w = 1/\sigma^2(F_o^2)$ . Scattering factors for Co, K<sup>+</sup>, S, C, N, and O were from ref 10, with the real part of anomalous dispersion being taken into account for Co and K<sup>+</sup>.

### Description of the Structure and Discussion

Positional and thermal parameters are given in Table II. The crystal structure of this salt consists of discrete potassium ions,

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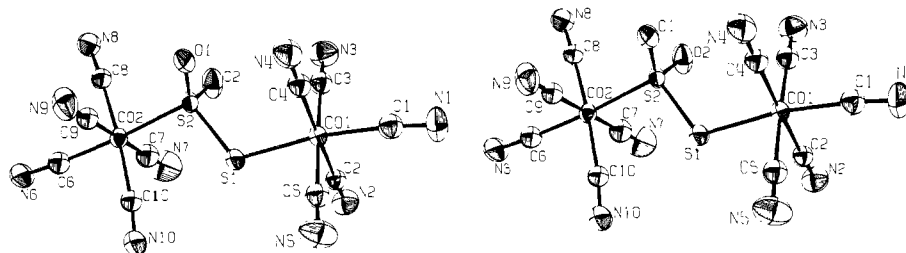


Figure 1. The decacyano- $\mu$ -(thiosulfito-*S,S'*)-dicobaltate(III) anion in stereopair. Atoms are represented by thermal ellipsoids enclosing 50% probability.

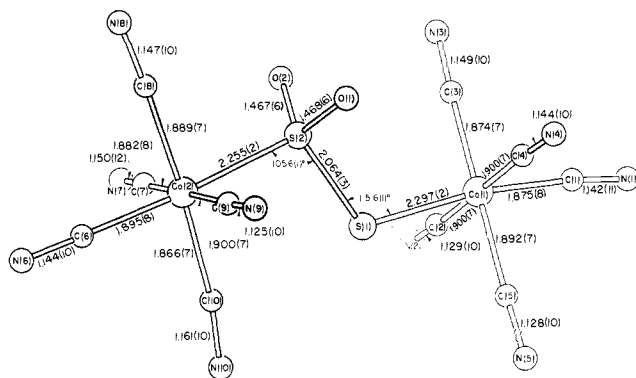


Figure 2. Interatomic distances and some important angles in the anion.

binuclear cobalt anions, and solvent molecules. One potassium ion and most of the solvent molecules are affected by disorder; however, the interesting part of the structure, the  $\mu$ -(thiosulfito-*S,S'*)-decacyanodicobaltate(III) ion, appears ordered and well-behaved.

We make no representation that our description of the solvent region is correct in even approximate detail; it is apparent that our diffraction data are incapable of resolving the complexities of the disorder. We note in particular that we obtained only slightly higher agreement indexes with a model which contained no ethanol and a quite different distribution of water molecules among partially occupied sites; we abandoned this model because of structural implausibilities. We take comfort in the fact that all the important results—the parameters of the cations and, particularly, the anion—remained the same within 2 esd's for the two refinements. A more ordered model might well be attained in space group *Cc*; however, it seems clear—particularly in light of our earlier experiences—that the near singularities in any such model would prevent meaningful refinement.

As far as we are aware, this is the first well-characterized example of the thiosulfite species  $\text{SSO}_2^{2-}$ ; it presumably formed by air oxidation of the dithio bridge in the binuclear anion  $\text{Co}_2\text{S}_2(\text{CN})_{10}^{6-}$ , the rest of the anion remaining undisturbed. A drawing of the thiosulfite complex is shown in Figure 1, and bond distances are given in Figure 2.

The two S–O bond distances are equal within experimental error and average at 1.468 (4) Å, marginally shorter than those found in the coordinated sulfites  $\text{Co}(\text{en})_2\text{SO}_3\text{SCN}^{11}$  (1.485 (9) Å) and  $\text{Pd}(\text{NH}_3)_3\text{SO}_3^{12}$  (1.494 (10) Å), and essentially equal to the 1.463 (2) Å found<sup>13</sup> in the S-bonded thiosulfate species  $[(\text{NH}_3)_5\text{CoS}_2\text{O}_3]^+$ . The S–O distance in ionic sulfites is typically in the range 1.51–1.53 Å. The S–S distance, at 2.064 (3) Å, is characteristic of a single bond, being essentially equal to the average values 2.07 (8) Å reported for a number of polysulfides and polythionates,<sup>14</sup> 2.04–2.07 Å reported for various allotropic forms of elemental sulfur,<sup>15</sup> and 2.063 (9) Å found in thiosulfate

complexes in which only the terminal sulfur atom is coordinated.<sup>13,16,17</sup> The unit Co–S–S–Co is planar, the torsion angle being 179.0 (1)°.

The Co–S(sulfite) bond, at 2.255 (2) Å, is appreciably shorter than the Co–S(thio) bond, 2.297 (2) Å, presumably due to a greater tendency toward  $\pi$ -acceptor behavior. A meaningful comparison of these values with Co(III)–S bond lengths in other compounds is complicated because of the wide variety of ligands, but we shall hazard a brief discussion.

The Co–S(sulfite) bond is somewhat longer than found in the cobalt-sulfite species  $(\text{en})_2\text{CoSO}_3\text{SCN}$ , 2.203 (6) Å,<sup>11</sup> and  $[(\text{NH}_3)_5\text{CoSO}_3]^+$ , 2.218 (2) Å.<sup>18</sup> Some, and perhaps all, of the difference is probably a consequence of competition for  $\pi$ -electron density, the CN groups in the present compound being much better  $\pi$  acceptors than  $\text{NH}_3$  and *en*. An estimate of this effect might be made by comparing the Co–S distance in the CN-coordinated species  $(\text{CN})_5\text{CoSCNCo}(\text{NH}_3)_5$ , 2.334 (2) Å,<sup>19</sup> with that in the ammine species  $[(\text{NH}_3)_5\text{CoSCN}]^{2+}$ , 2.272 (7) Å,<sup>20</sup> but this comparison is marred by the difference in coordination of the SCN group.

The Co–S(thio) bond, at 2.297 (2) Å, is longer than in the ammine complexes  $(\text{NH}_3)_5\text{CoSCN}$ , 2.272 (7) Å,<sup>20</sup>  $[(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ , 2.226 Å,<sup>21</sup> and  $[(\text{en})_2\text{CoSCH}_2\text{CO}_2]^{2+}$ , 2.243 (2) Å;<sup>21</sup> the  $\pi$  competition mentioned above might well explain most of the difference. Comparison with the 2.334 (2) Å<sup>19</sup> in  $(\text{CN})_5\text{CoSCNCo}(\text{NH}_3)_5$  is more straightforward and suggests that the Co–S(thio) bond is inherently stronger than Co–SCN. It is probably also stronger than the Co–SSO<sub>3</sub> bond, as represented by the ammine thiosulfate  $[(\text{NH}_3)_5\text{CoS}_2\text{O}_3]^+$ , 2.287 (1) Å,<sup>13</sup> even though the Co–S(thio) bond is longer; the effect of the CN<sup>−</sup> ligands on the Co–S(thio) bond must be considered. All these examples, then, tend to confirm an appreciable tendency for  $\pi$  character in the Co–S(thio) bond and, of course, even more for the Co–S(sulfite) bond.

The possibility of a trans effect in octahedral Co(III)–S compounds has been discussed previously,<sup>13,21</sup> such an effect is evident in a lengthening of Co–N bonds in ammines and *en* groups trans to S, but its magnitude appears to vary widely. The effect should be quite different for trans Co–CN bonds, because of the strong  $\pi$ -bonding capability of cyanide; indeed, there appears to be a marginally significant *shortening*, by 0.025 (8) Å, of the trans Co–C bond in  $(\text{CN})_5\text{CoSCNCo}(\text{NH}_3)_5$ , suggesting that S-bonded thiocyanate has difficulty competing with CN for these electrons. In the present compound the trans effects at the two Co atoms are even smaller, but the trend is in the direction that we might expect. Thus, the bond trans to Co–S(thio), Co(1)–C(1), is a bit shorter than the average of the other Co(1)–C bonds—1.875 (8) vs. 1.892 (6) Å—while the bond trans to the Co–S(thiosulfite) bond may be longer than the other Co(2)–C bonds—1.895 (8)

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Table III. Bonding Angles (Deg)

S(1)-Co(1)-C(1)	171.3 (2)	S(2)-Co(2)-C(6)	175.9 (2)
-C(2)	87.3 (2)	-C(7)	89.4 (3)
-C(3)	98.1 (2)	-C(8)	87.6 (2)
-C(4)	93.2 (2)	-C(9)	89.6 (2)
-C(5)	83.3 (2)	-C(10)	97.4 (2)
C(1)-Co(1)-C(2)	88.9 (3)	C(6)-Co(2)-C(7)	92.2 (3)
-C(3)	89.7 (3)	-C(8)	88.5 (3)
-C(4)	90.6 (3)	-C(9)	88.9 (3)
-C(5)	88.8 (3)	-C(10)	86.5 (3)
C(2)-Co(1)-C(3)	88.8 (3)	C(7)-Co(2)-C(8)	91.9 (3)
-C(4)	179.3 (3)	-C(9)	178.6 (3)
-C(5)	89.7 (3)	-C(10)	88.7 (3)
C(3)-Co(1)-C(4)	90.6 (3)	C(8)-Co(2)-C(9)	89.1 (3)
-C(5)	177.9 (3)	-C(10)	175.0 (3)
C(4)-Co(1)-C(5)	90.9 (3)	C(9)-Co(2)-C(10)	90.4 (3)
Co(1)-C(1)-N(1)	175.3 (7)	Co(2)-C(6)-N(6)	175.2 (7)
-C(2)-N(2)	178.7 (6)	-C(7)-N(7)	177.3 (8)
-C(3)-N(3)	177.7 (7)	-C(8)-N(8)	176.2 (6)
-C(4)-N(4)	178.0 (7)	-C(9)-N(9)	176.6 (7)
-C(5)-N(5)	178.7 (7)	-C(10)-N(10)	173.1 (7)
Co(1)-S(1)-S(2)	115.6 (1)		
Co(2)-S(2)-S(1)	105.6 (1)		
-O(1)	111.9 (2)		
-O(2)	111.5 (2)		
S(1)-S(2)-O(1)	109.3 (2)		
-O(2)	108.5 (2)		
O(1)-S(2)-O(2)	109.9 (3)		

vs. 1.884 (7) Å. In any event, it appears that both the S(thio) and the S(thiosulfito) atoms can compete quite successfully with CN for the  $\pi$  electrons.

The ten C-N distances range from 1.125 (10) to 1.161 (10) Å and average 1.142 (4) Å. All cyanides coordinate in the usual "linear" fashion, with deviations from linearity of less than 7°. These angles, as well as others of importance, are listed in Table III. All cyanide ligands coordinate to cobalt via their carbon atoms, as is shown by the reasonable temperature factors of the atoms involved.

The anion could have maximum symmetry  $C_s$  (mirror), but in the crystal it lies in a general position and the deviations from idealized symmetry are very large. Actually, the  $(CN)_5CoSO_2S$  unit conforms fairly well to  $C_s$  symmetry, but the rotameric configuration of the other pentacyanocobalt grouping is approximately at maximum deviation from either of the two  $C_s$  positions.

A description of the crystal packing is somewhat confused by the disorder and partial occupancy associated with K(7) and most of the solvent molecules. In general, the highly charged anions are well separated from each other by an envelope of potassium counterions and water molecules hydrogen bonded to them and to each other. Each anion has contacts of less than 3.4 Å to 22  $K^+$  ions and to 23 sites of at least partial occupancy by water or ethanol molecules.

The potassium ions are surrounded primarily by cyanide ligands and solvent molecules, with occasional contacts to sulfito oxygen atoms. All contact distances are at least 2.6 Å. If we take into account the population factors of the various solvent molecules, the coordination numbers range from 6 to 8 except for the disordered atom K(7), with a coordination number of only 4.6—a number more attractive to the water molecule W(5) which shares the same general site. The substitutional disorder involving K(7)

Table IV. Contacts (Å) Less than 3.4 Å to the Potassium Ions

K(1)-N(4)	2.823 (7)	K(5)-N(4)	3.054 (7)
-N(6) <sup>a</sup>	3.011 (8)	-N(9)	3.008 (7)
-N(8) <sup>a</sup>	3.233 (7)	-N(8) <sup>a</sup>	3.036 (7)
		-N(9) <sup>k</sup>	3.377 (7)
K(2)-N(6)	2.862 (7)	-O(1)	2.772 (6)
-N(9) <sup>b</sup>	2.746 (7)	-O(1) <sup>k</sup>	2.928 (6)
-N(3) <sup>c</sup>	2.946 (8)	-W(4)	2.652 (10)
-N(5) <sup>d</sup>	2.806 (8)	-W(2) <sup>l</sup>	2.874 (9)
-O(1) <sup>c</sup>	2.790 (6)		
-O(2) <sup>c</sup>	3.384 (6)	K(6)-N(2)	2.886 (7)
-W(2) <sup>e</sup>	2.950 (9)	-N(8) <sup>i</sup>	3.201 (7)
		-N(10) <sup>f</sup>	3.007 (7)
K(3)-N(2)	3.218 (7)	-N(1) <sup>g</sup>	2.803 (8)
-N(7)	3.313 (9)	-O(2) <sup>i</sup>	2.731 (6)
-N(2) <sup>f</sup>	2.923 (7)	-W(3) <sup>g</sup>	2.915 (8)
-O(2)	2.740 (6)	-W(5A) <sup>c</sup>	3.10 (2)
-W(5C) <sup>g</sup>	3.17 (3)	-W(5B) <sup>c</sup>	3.10 (3)
-W(3) <sup>g</sup>	2.739 (8)		
-Et(O2) <sup>h</sup>	3.128 (n)	K(7)-N(1)	2.973 (10)
-W(5A) <sup>c</sup>	2.74 (2)	-N(1) <sup>g</sup>	3.003 (10)
-W(5B) <sup>c</sup>	3.30 (3)	-N(7) <sup>a</sup>	2.790 (10)
-W(5C) <sup>c</sup>	2.84 (3)	-W(8) <sup>f</sup>	2.761 (17)
		(-W(6) <sup>j</sup> ) <sup>o</sup>	2.617 (6)
K(4)-N(8) <sup>i</sup>	2.957 (7)	(-W(6) <sup>m</sup> )	3.329 (6)
-N(6) <sup>b</sup>	3.307 (8)	-W(5B) <sup>c</sup>	3.13 (3)
-N(10) <sup>f</sup>	2.932 (7)		
-N(4) <sup>g</sup>	3.294 (7)		
-N(5) <sup>g</sup>	3.347 (8)		
-W(1) <sup>j</sup>	2.861 (7)		
-Et(O1) <sup>j</sup>	2.892 (n)		
-W(1) <sup>c</sup>	2.791 (7)		

<sup>a</sup>  $x, -y, -1/2 + z$ . <sup>b</sup>  $-x, y, 3/2 - z$ . <sup>c</sup>  $x, -y, 1/2 + z$ . <sup>d</sup>  $x, 1 - y, 1/2 + z$ . <sup>e</sup>  $x, y, 1 + z$ . <sup>f</sup>  $1/2 - x, -1/2 + y, 3/2 - z$ . <sup>g</sup>  $1/2 - x, 1/2 - y, 1 - z$ . <sup>h</sup>  $1 - x, y, 3/2 - z$ . <sup>i</sup>  $1/2 - x, 1/2 + y, 3/2 - z$ . <sup>j</sup>  $1 - x, -y, 1 - z$ . <sup>k</sup>  $-x, -y, 1 - z$ . <sup>l</sup>  $-x, y, 1/2 + z$ . <sup>m</sup>  $1/2 + x, 1/2 + y, z$ . <sup>n</sup> ESD not determined. <sup>o</sup> At any given site, either one or the other of these atoms (but not both) is present.

and W(5) is not unique to this structure; a similar disorder between  $K^+$  and  $H_2O$  also occurs in crystals of the related compound  $K_5[(CN)_5Co_2OCo(CN)_5] \cdot H_2O$ .<sup>22</sup>

The severe disorder associated with the solvent region precludes any reasonable discussion of hydrogen bonding or other packing forces. We reiterate that our description of this region may well be inappropriate; it has the virtue that no nonbonded distance need be shorter than a normal hydrogen bond, a feature that is difficult to attain while satisfying the demands of the Fourier maps. The primary purpose of solvent in this crystal appears to be to occupy the voids left by the packing of the ionic species; presumably these voids are not in all cases of the appropriate size or shape, so that disorder of the solvent results.

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**Registry No.**  $K_6[CO_2SSO_2(CN)_{10}] \cdot xH_2O \cdot x(C_2H_5OH)$ , 81611-01-0.

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