conformations should allow estimates of these π-bond energies and will be reported in a later paper.

The second form of evidence suggesting multiple bonding between the metal atom and the pyridine groups comes from the metal–nitrogen atom bond lengths. The values determined here are nearly equal and average 2.187 Å. Values of 2.12 and 2.14 Å have been reported for this distance in $Co(NCS)_2(py)_2$[28] and $CoCl_2(py)_2$,[29] where the cobalt atom in both cases is octahedrally coordinated through bridging by the nonpyridine ligands; however, both of these structures were done only with projections and no reliable estimate of the errors involved is available. Further, these distances might also be shortened from the ideal single-bond distance. The value for hypothetical single-bond distances for the fifth and sixth coordination positions of a cobalt acetylacetonate is needed, and the structure[6] of $Co(AA)_2(H_2O)_2$ provides that information. There is little reason to believe that there is any double bonding between the cobalt atom and the water molecule; thus the $Co–O_{H_2O}$ distance of 2.23 ± 0.01 Å may be taken to represent the single bond distance between cobalt and oxygen atoms of neutral molecules in cobalt acetylacetonate adducts. In going from oxygen to nitrogen a correction[30] of 0.04 Å must be added to give the expected cobalt–nitrogen atom distance of 2.27 Å. Thus the distance, 2.187 Å, determined in this study seems to indicate some shortening due to π bonding.

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[29] J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

[30] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224 f. Table 7.2 lists the covalent radius for the nitrogen atom as 0.70 Å and that for the oxygen atom as 0.66 Å, whereas Table 7.5 gives the Schomaker–Stevenson radii of both atoms as 0.74 Å; however, the second distances must be corrected for electronegativity differences between cobalt and nitrogen or oxygen by -0.09 Å $|\chi_{Co} - \chi_{N,O}|$, which gives nitrogen as 0.045 Å larger than oxygen.

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of π-Cyclopentadienyl(1,2-dicyanoethene-1,2-dithiolato)cobalt[1,2]

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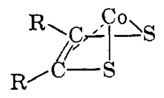
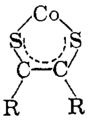
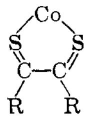
π-Cyclopentadienyl(1,2-dicyanoethene-1,2-dithiolato)cobalt, π-$C_5H_5CoS_2C_2(CN)_2$, crystallizes in the monoclinic space group C2/c (C_{2h}^6; no. 15) with $a = 17.05 \pm 0.02$ Å, $b = 8.50 \pm 0.01$ Å, $c = 14.82 \pm 0.02$ Å, $\beta = 109.48 \pm 0.05°$, $Z = 8$. Observed and calculated densities are, respectively, 1.72 ± 0.02 and 1.732 g cm^{-3}. A single-crystal X-ray diffraction study, based on data to $\sin \theta = 0.40$, has led to the location of all atoms (including hydrogens). The final discrepancy index is $R_F = 7.1\%$ for 1337 independent nonzero reflections. The crystal is composed of distinct molecular units of π-$C_5H_5CoS_2C_2(CN)_2$ separated by normal van der Waals forces. The cobalt atom may be considered pentacoordinate since it is linked to a bidentate dithiolate ligand and a formally tridentate π-cyclopentadienyl ligand. The molecule possesses approximate C_s symmetry. Cobalt–sulfur distances average 2.117 ± 0.003 Å; other distances within the dithiolate system include: C–S = 1.702 ± 0.007 Å and C–C = 1.364 ± 0.010 Å.

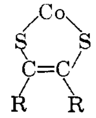
Introduction

Infrared spectral studies on the 1,2-disubstituted ethene-1,2-dithiolate complexes, π-$C_5H_5CoS_2C_2R_2$ (R = CF_3,[3] CN[4]), led to the suggestion that the dithiolate ligand might bond to the metal *via* both cobalt–sulfur and cobalt–olefin bonding (I), rather than by cobalt–sulfur bonding alone (II). A crystallographic examination of π-$C_5H_5CoS_2C_2(CN)_2$ was originally[5] undertaken to resolve this ambiguity. However, while our investigation of the complex was still incomplete, a study[6] of the closely related molecule π-$C_5H_5CoS_2C_2(CF_3)_2$ showed structure II to be appropriate. The bond distances within the $S_2C_2(CF_3)_2$ ligand (particularly the carbon–carbon bond length of 1.48 ± 0.05 Å within the "ethene") led to the proposal[6] that the molecule should be described as an ethane-1,2-dithione complex (III) rather than as an ethylene-1,2-dithiolate de-


I


II


III


IV

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[1] We have followed Ibers[2] in using the term "ethene-1,2-dithiolate" to describe the ligand in such a way as not to predispose the reader toward any one valence bond description of the complex. The structural formula II is in keeping with this policy.

[2] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966), particularly footnote 20.

[3] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[4] J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).

[5] See footnote 17 of ref 4.

[6] H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).

rivative (IV). Since crystallographic studies on a variety of bis and tris transition metal complexes of 1,2-disubstituted ethene-1,2-dithiolates had shown[2,7–16] carbon–carbon bond lengths within the "ethene" residue to vary in the range 1.32–1.40 Å (*i.e.*, closer to an ethylene bond length of 1.335 Å[17a] than to an sp^2–sp^2 single-bond distance of 1.465[17b]) we decided to continue our structural study of π-$C_5H_5CoS_2C_2(CN)_2$. Our results are summarized below.

Unit Cell and Space Group

Purple-black crystals of π-$C_5H_5CoS_2C_2(CN)_2$ were supplied by Dr. J. A. McCleverty[4] of Sheffield University, Sheffield, England. The complex is air stable and is not X-ray sensitive. Optical examination and a reciprocal lattice symmetry of C_{2h} (2/m) indicated that the crystals belonged to the monoclinic system. Unit-cell dimensions at 24 ± 2°, obtained by a least-squares analysis of calibrated ($a_{NaCl} = 5.640$ Å) high-angle precession data taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) are: $a = 17.05 \pm 0.02$ Å, $b = 8.50 \pm 0.01$ Å, $c = 14.82 \pm 0.02$ Å, $\beta = 109.48 \pm 0.05°$. The unit-cell volume is 2024 Å^3. A survey of *Nkl*, *hNl*, *hkN* (N = 0–2) photographs revealed the systematic absences *hkl* for $h + k = 2n + 1$ and *h0l* for $l = 2n + 1$, compatible with space group Cc (no. 9) or C2/c (no. 15). The observed density ($\rho_{obsd} = 1.72 \pm 0.02$ g cm^{-3}, by flotation in aqueous zinc iodide solution) indicated eight molecules per unit cell ($\rho_{calcd} = 1.732$ g cm^{-3} for $M = 264$, $Z = 8$). The Patterson synthesis and subsequent solution of the structure (*vide infra*) showed that the true space group was the centrosymmetric C2/c (C_{2h}^6; no. 15).

Collection and Reduction of X-Ray Data

Two crystals were used for data collection: crystal I (0.30 × 0.38 × 0.15 mm) was mounted on its a axis and crystal II (0.40 × 0.32 × 0.10 mm) was mounted on its b axis. Intensity data were collected with a 0.01°-incrementing Buerger automated diffractometer, used in conjunction with a fully stabilized Philips X-ray generator (operated at 47 kV/15 mA), a Philips No. 52572 transistorized scintillation counter, and a Philips No. 12206 electronics panel. The scintillation counter was adjusted to receive Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å), the Kβ component being virtually eliminated by the use of a 0.003-in. zirconium filter at the X-ray source. With the counter voltage stabilized at 840 V, the base line of the pulse-height analyzer and the window voltage were optimized by monitoring an intense reflection on a standard (sodium chloride) crystal. All voltages were then maintained at constant values throughout the analysis.

Reciprocal-lattice and diffractometer coordinates were brought into coincidence after determining the counter angle (Υ) and crystal-rotation angle (Φ) for a series of Friedel-related reflections on the levels *0kl* (crystal I) and *h0l* (crystal II). Background radiation was reduced to the minimum level compatible with no loss of intensity in the diffracted beam by interposing a series of 2.0-mm lead-surrounded apertures in the collimating system between crystal and counter. The source-to-crystal distance was 70 mm and the crystal-to-counter distance was 90 mm. No attenuators were used since the maximum observed counting rate ($\sim 2 \times 10^4$ counts/sec) was not expected to give rise to coincidence losses (the "dead-time" of the counter is less than 10^{-6} sec).

The diffractometer was programmed to collect all data within a given Weissenberg zone using the standard "stationary-background, ω-scan, stationary-background" counting sequence. A careful study of the mosaicity of the two crystals led to the choice of scan range $\omega = [2.0 + (0.6/L)]°$, where $1/L$ is the Lorentz factor for the equiinclination Weissenberg method, $1/L = \cos^2 \mu \sin \Upsilon$. [The inclusion of the term involving the Lorentz factor allows for the divergence of the X-ray beam, which manifests itself in extended low-order reflections on upper-level data.[18]] Within each zone, the over-all stability of the entire system (and the setting of the crystal) was monitored by remeasuring a carefully selected check reflection after each batch of 20 reflections had been collected; also, the check reflection for the appropriate zero layer was remeasured at the end of each zone. The absence of any significant variations indicated stability both of electronics *and* sample. Throughout the analysis, all scans were recorded on a chart recorder in order to check on peak profile, centering of the reflection in ϕ, and possible overlap of adjacent reflections. No such problems were, in fact, encountered.

$I(hkl)$, the intensity of a reflection *hkl*, was determined in the following manner. (i) The counter was positioned to $\Upsilon_0(hkl)$ where it remained stationary. (ii) The crystal was rotated to an angle $\phi_1 = [\Phi_0(hkl) - \omega(hkl)/2]$ and the first background, B_1, was measured for t sec. (iii) The crystal was rotated by $\omega(hkl)°$ at a constant rate of 1°/min until it reached the angle $\phi_2 = [\Phi_0(hkl) + \omega(hkl)/2]$. The entire scan took $2t$ sec, the integrated count being C. (iv) The second background, B_2, was measured for t sec at ϕ_2. (v) The net count was calculated as $I(hkl) = C - (B_1 + B_2)$.

Long-exposure Weissenberg photographs for the zones *Nkl* and *hNl* (N = 0–2) indicated that beyond $\sin \theta = 0.40$ there was a very low ratio of observable to unobservable reflections. It was decided, therefore, to restrict data collection to those reflections with $\sin \theta \leqslant 0.40$. Data for the zones *0kl* through *18kl* were col-

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR π-$C_5H_5CoS_2C_2(CN)_2$ (IN ELECTRONS)

K	L	FO	FC
H = 0			
0	4	-244	-229
0	6	152	143
0	8	-32	-19
0	10	-73	-73
0	12	100	97
0	14	-19	-10
2	0	-134	-123
2	1	0	83
2	2	49	42
2	3	0	-14
2	4	154	150
2	5	2	6
2	6	14	9
2	7	0	-48
2	8	-8	-5
2	9	-1	9
2	10	87	92
2	11	-3	-8
2	12	-51	-50
2	13	-3	4
2	14	-47	-46
4	0	281	275
4	1	-1	-27
4	2	-85	-75
4	3	1	-34
4	-4	-124	-111
4	5	0	-35
4	6	137	137
4	7	1	-16
4	8	-60	-61
4	9	0	20
4	10	-53	-48
4	11	-1	22
4	12	72	68
4	-13	9	10
6	0	-81	-75
6	1	0	33
6	2	-16	-12
6	3	0	37
6	4	24	24
6	5	0	13
6	6	-13	-2
6	7	-1	-20
6	8	4	4
6	9	0	-11
6	10	43	39
6	11	7	-21
6	12	-31	-28
8	0	62	57
8	1	1	-23
8	2	-36	-34
8	3	0	-8
8	4	-37	-32
8	5	1	-10
8	6	57	50
8	-7	-4	-1
8	8	-36	-32
H = 1			
1	2	-45	-36
1	3	-105	-98
1	4	-27	-28
1	-4	92	81
1	5	-22	-20
1	-5	18	14
1	6	-28	-29
1	-6	-88	-81
1	7	161	158
1	-7	32	25
1	8	45	33
1	-8	30	29
1	9	-73	-71
1	-9	-37	-38
1	10	-25	-27
1	-10	12	7
1	11	-101	-98
1	-11	104	102
1	-12	-25	-7
1	13	43	42
1	-13	-17	-15
1	14	23	20
1	-14	13	16
1	15	28	26
1	-15	-59	-54
3	0	-140	-140
3	1	-175	-176
3	-1	9	10
3	2	34	35
3	-2	-11	-7
3	-3	116	113
3	4	8	4
3	-4	77	72
3	5	28	27
3	-5	-151	-138
3	6	-12	-11
3	-6	-24	-23
3	7	-105	-110
3	-7	-25	-24
3	8	47	46
3	-8	10	8
3	9	36	39
3	-9	52	53
3	10	-22	-23
3	-10	14	14
3	11	71	76
3	-11	-67	-69
3	12	-17	-13
3	-12	-33	-35
3	13	-37	-35
3	-13	-19	-18
3	14	5	9
3	-14	13	12
3	-15	47	47
5	0	5	11
5	1	118	117
5	-1	-101	-98
5	2	74	73
5	-2	26	24
5	3	-42	-39
5	-3	-138	-132
5	4	4	4
5	-4	-16	-17
5	5	-37	-40
5	-5	66	67
5	6	-47	-43
5	-6	-67	-61
5	7	72	72
5	-7	-17	-17
5	8	-13	-11
5	-8	-12	-5
5	9	-35	-34
5	-9	-44	-44
5	10	-16	-15
5	-10	5	4
5	11	-52	-43
5	-11	56	53
5	12	19	20
5	-12	3	0
5	13	20	26
5	-13	-13	-1
7	0	-58	-57
7	1	-70	-68
7	-1	44	42
7	2	23	22
7	-2	-5	-5
7	3	-23	-21
7	-3	64	57
7	4	8	8
7	-4	41	34
7	5	29	25
7	-5	-53	-48
7	6	7	7
7	-6	-13	-3
7	7	-26	-27
7	-7	-25	-24
7	8	33	36
7	-8	7	4
7	-9	35	32
7	10	-4	-7
H = 2			
0	2	-157	-159
0	4	53	57
0	6	16	14
0	-6	-59	-48
0	8	-196	-200
0	-8	106	93
0	10	67	72
0	-10	-106	-112
0	12	34	26
0	-12	27	24
0	14	-23	-16
0	-14	62	60
0	-16	-24	-29
2	0	-89	-88
2	1	30	29
2	-1	103	98
2	2	-100	-97
2	-2	-128	-129
2	3	39	43
2	-3	-18	-19
2	4	-8	-8
2	-4	75	72
2	5	-19	-20
2	-5	-17	-14
2	6	-20	-22
2	-6	55	53
2	7	17	19
2	-7	18	15
2	8	80	90
2	-8	-97	-96
2	9	-11	-11
2	-9	9	10
2	10	17	14
2	-10	14	13
2	11	7	7
2	-11	-8	-6
2	12	-64	-59
2	-12	26	29
2	13	-15	-10
2	-13	-11	-1
2	-14	-74	-78
2	-15	-16	-5
4	0	110	110
4	1	31	30
4	-1	46	44
4	2	-146	-154
4	-2	138	139
4	3	-8	-6
4	-3	84	86
4	4	79	84
4	-4	-215	-219
4	5	-35	-33
4	-5	10	7
4	6	14	18
4	-6	14	15
4	7	-13	-12
4	-7	-22	-17
4	8	-118	-120
4	-8	82	81
4	9	33	36
4	-9	-27	-29
4	10	39	40
4	-10	-73	-74
4	11	9	11
4	12	36	33
4	-12	11	12
4	13	6	1
4	-14	42	40
6	0	-12	-13
6	1	8	9
6	-1	-11	-12
6	2	21	22
6	-2	-49	-51
6	3	47	47
6	-3	-49	-47
6	4	-18	-18
6	-4	41	42
6	5	23	25
6	-5	13	2
6	6	-37	-36
6	-6	65	65
6	7	6	4
6	-7	40	39
6	8	49	48
6	-8	-22	-24
6	9	-15	-14
6	-9	18	18
6	10	27	23
6	-10	9	8
6	11	-16	-10
6	-11	-10	-7
8	0	30	30
8	1	-6	-5
8	-1	5	4
8	2	-70	-69
8	-2	55	54
8	3	-9	-8
8	-3	26	27
8	4	46	42
8	-4	-54	-53
8	5	-11	-11
8	-5	14	6
8	6	24	22
8	-6	13	13
8	7	-16	-10
8	-7	-8	-1
8	-8	26	31
H = 3			
1	1	-24	-22
1	2	113	113
1	3	-118	-115
1	4	-34	-35
1	-4	182	177
1	5	120	120
1	-5	-30	-25
1	6	44	43
1	-6	17	17
1	7	124	121
1	-7	178	169
1	8	-17	-5
1	-8	-51	-45
1	9	-107	-108
1	-9	27	21
1	10	-38	-33
1	-10	51	48
1	11	-29	-29
1	-11	-24	-23
1	12	23	17
1	-12	-11	-12
1	13	17	15
1	-13	41	42
1	14	8	4
1	-14	11	8
1	-15	-43	-42
1	-16	13	5
3	0	-23	-14
3	1	-74	-71
3	-1	-26	-25
3	2	-2	-2
3	-2	-16	-18
3	3	74	77
3	-3	204	205
3	4	-23	-26
3	-4	113	114
3	5	-76	-79
3	-5	61	57
3	6	36	36
3	-6	-10	-6
3	7	-43	-48
3	-7	-127	-121
3	8	32	36
3	-8	7	4
3	9	70	70
3	-9	51	51
3	10	-31	-30
3	-10	22	24
3	11	7	9
3	-11	37	43
3	12	13	10
3	-12	-20	-20
3	13	-37	-35
3	-13	-44	-42
3	-14	-12	-6
3	-15	21	27
5	0	19	19
5	1	16	19
5	-1	71	67
5	2	77	78
5	-2	-43	-42
5	3	-70	-76
5	-3	-115	-115
5	4	-16	-13
5	-4	8	9
5	5	79	77
5	-5	18	17
5	6	-16	-17
5	-6	-58	-55
5	7	52	43
5	-7	96	94
5	8	-17	-11
5	-8	-20	-19
5	9	-69	-63
5	-9	-22	-20
5	10	-32	-30
5	-10	57	56
5	-11	10	8
5	12	24	23
5	-12	6	6
5	-13	36	37
5	-14	13	4
7	0	-20	-21
7	1	-7	-5
7	-1	-5	-3
7	2	-14	-12
7	-2	-35	-35
7	3	22	20
7	-3	56	56
7	4	-20	-22
7	-4	40	38
7	5	-26	-26
7	-5	-11	-7
7	6	15	16
7	-6	4	2
7	7	-25	-27
7	-7	-51	-48
7	8	30	27
7	-8	-10	-0
7	9	35	30
7	-9	30	28
7	-10	6	4
9	0	4	7
9	1	16	16
9	-1	27	26
9	2	26	24
9	-2	-4	-9
9	3	-39	-36
9	-3	-32	-32
H = 4			
0	2	153	155
0	4	249	256
0	-4	-171	-173
0	6	-182	-186
0	-6	-105	-108
0	8	-80	-80
0	-8	171	171
0	10	83	74
0	-10	33	26
0	12	-26	-24
0	-12	-46	-39
0	14	-15	-14
0	-14	67	70
0	-16	6	3
2	0	-42	-40
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4	-2	-14	-16
4	3	8	6
4	-3	-18	-21
4	4	27	25
4	-4	-86	-87
4	-5	-9	-7
4	6	59	55
4	-6	57	59
4	-7	7	15
4	-8	45	45
4	-9	-14	-14
4	-10	-35	-35
4	-11	4	4
4	-13	16	16
6	0	-11	-9
6	1	-40	-39
6	-1	3	2
6	2	19	19
6	-2	-22	-21
6	3	-17	-7
6	-3	17	11
6	-4	37	34
6	-5	14	15
6	-6	-10	-2
6	-7	3	1
6	-8	-50	-51
6	-9	-9	-10
6	-10	25	26
H = 13			
1	0	-45	-43
1	1	12	11
1	-1	25	24
1	2	10	13
1	-2	-30	-26
1	3	-77	-69
1	-3	-42	-40
1	4	-22	-19
1	-4	21	21
1	5	14	13
1	-5	41	40
1	6	-14	-11
1	-6	-50	-50
1	7	42	32
1	-7	58	54
1	-8	23	24
1	-9	-67	-62
1	-10	29	29
1	-11	-20	-20
1	-12	-22	-23
1	-13	33	31
1	-15	-16	-18
3	0	-31	-30
3	1	13	14
3	-1	-30	-29
3	2	19	19
3	-2	18	17
3	3	66	64
3	-3	27	26
3	4	-21	-19
3	-4	36	40
3	5	-6	-6
3	-5	-62	-57
3	6	-24	-19
3	-6	-61	-58
3	-7	-54	-50
3	-8	-12	-11
3	-9	61	60
3	-10	19	20
3	-11	30	25
3	-12	-14	-10
3	-13	-36	-33
3	-14	10	12
5	0	-25	-23
5	1	23	21
5	-1	22	21
5	2	31	29
5	-2	-14	-13
5	3	-54	-49
5	-3	-40	-39
5	-4	11	12
5	-5	19	19
5	-6	-7	-5
5	-7	43	40
5	-8	16	16
5	-9	-35	-32
5	-10	16	11
5	-11	-15	-16
H = 14			
0	0	-31	-21
0	2	-56	-56
0	-2	52	52
0	4	88	79
0	6	11	7
0	-6	-18	-15
0	-8	76	77
0	-10	-20	-20
0	-12	-26	-26
0	-14	8	10
2	0	69	70
2	-1	12	10
2	2	25	26
2	-2	-17	-22
2	3	-13	-14
2	-3	33	31
2	4	-44	-39
2	-4	-10	-8
2	-5	11	9
2	6	-9	-10
2	-6	49	52
2	-7	10	8
2	-8	-70	-67
2	-9	-10	-8
2	-10	-34	-32
2	-11	-10	-5
2	-12	65	63
2	-13	-9	-7
2	-14	-9	-8
4	0	-33	-31
4	1	5	6
4	-1	6	0
4	2	-37	-36
4	-2	31	29
4	3	31	29
4	-3	6	7
4	4	63	58
4	-4	-29	-32
4	-5	-8	-3
4	-6	9	7
4	-7	7	7
4	-8	61	62
4	-9	6	4
4	-10	-10	-11
4	-12	-26	-28
6	0	23	26
6	-1	-6	-2
6	-2	-17	-21
6	-3	14	18
6	-4	-10	-8
6	-5	10	12
6	-6	37	41
6	-7	6	8
6	-8	-23	-25
H = 15			
1	0	9	7
1	1	-52	-46
1	-1	61	55
1	2	10	10
1	-2	-21	-21
1	3	-48	-41
1	-3	12	9
1	-4	43	39
1	-5	-29	-29
1	-6	15	8
1	-7	51	45
1	-8	-10	-7
1	-9	-12	-12
1	-10	24	27
1	-11	-49	-46
3	0	22	20
3	1	35	35
3	-2	-6	-6
3	-3	-24	-23
3	-4	31	30
3	-6	-24	-24
3	-7	-49	-41
3	-8	-34	-34
3	-9	21	20
3	-10	40	37
H = 16			
0	0	-102	-88
0	-2	12	11
0	-4	17	15
0	-6	-31	-29
0	-8	23	20
0	-10	19	18
2	0	50	45
2	-1	14	14
2	-2	9	10
2	-3	8	6
2	-4	-73	-67
2	-6	18	18
2	-7	-10	-11
2	-8	7	5
2	-9	-17	-11
2	-10	-65	-62
H = 17			
1	-2	-10	-11
1	-3	65	57
1	-4	7	1
1	-5	-20	-20
1	-6	24	23
1	-7	-17	-15
1	-8	-25	-22

lected from crystal I and data for the zones $h0l$ through $h8l$ were collected from crystal II.

Standard deviations were assigned according to: $I(hkl) \geqslant 3[C + B_1 + B_2]^{1/2}$, $\sigma(hkl) = 0.1[I(hkl)]$; $I(hkl) \leqslant 3[C + B_1 + B_2]^{1/2}$, $\sigma(hkl) = 0.3[C + B_1 + B_2]/[I(hkl)]$; $I(hkl) \leqslant 0$, reflections rejected. Of the 1383 independent reflections measured from crystal I, 143 were rejected; 1142 nonzero reflections were obtained from the b-mounted crystal II. Data were corrected for Lorentz and polarization effects $[1/LP = 2\cos^2\mu \sin \Upsilon/(1 + \cos^2 2\theta)]$ and an absorption correction[19] (μ = 22.5 cm^{-1} for Mo Kα) was applied. Calculated transmission coefficients ranged from 0.51 to 0.71 for crystal I (volume 0.0138 mm^3) and from 0.52 to 0.80 for crystal II (volume 0.0108 mm^3).

Data were merged by means of a least-squares analysis[20] of common reflections. The resulting 1337 independent nonzero reflections were used for a Wilson plot, from which were obtained an approximate absolute scale factor and an over-all thermal parameter (B = 3.4 Å^2). [It should be noted that (due to the C-face-centering operation) there are no cross terms between $(2n + 1)h$ $(2n + 1)k$ l and $2nh$ $2nk$ l reflections. These two groups of reflections were treated separately. For the purposes of the Wilson plot it was assumed that the two groups of data were on a common scale; during

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(19) Using GNABS, a general absorption program by C. W. Burnham.

(20) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

subsequent refinement of the structure, two scale factors were included. These did not differ by more than 0.2% at the end of the refinement procedure.]

Elucidation and Refinement of Structure

A systematic survey of the three-dimensional normal-sharpened[21] Patterson synthesis,[22] $P(UVW)$, revealed a set of vectors compatible with a cobalt atom at $x = 0.098$, $y = -0.247$, $z = 0.159$ in the centrosymmetric space group C2/c. A three-dimensional difference-Fourier map,[22] phased by the cobalt atom ($R_F = 0.39$[23]), provided the locations of the two sulfur atoms. A second difference-Fourier synthesis, phased now by all three "heavy" atoms ($R_F = 0.28$), led to the location of all nonhydrogen atoms. Five cycles of refinement[24] of positional and individual isotropic thermal parameters for all nonhydrogen atoms resulted in convergence at $R_F = 0.115$, $R_{F^2} = 0.165$, $R_{wF^2} = 0.356$. A difference-Fourier synthesis now revealed patterns about some atomic positions characteristic of anisotropy in thermal motions (and also showed probable locations for hydrogen atoms, but these were temporarily ignored). Refinement was continued using anisotropic thermal parameters for all atoms. Two cycles of least-squares refinement led to the values $R_F = 0.086$, $R_{F^2} = 0.139$, $R_{wF^2} = 0.285$. A difference-Fourier map at this stage was relatively smooth in relief but showed peaks of height 0.5–0.7 e^- Å^{-3} in positions consistent with those expected for the five hydrogen atoms of the π-cyclopentadienyl ring [Peak heights for carbon atoms in a total electron density synthesis are each ~5 e^- Å^{-3}.] Contributions from hydrogen atoms were included in subsequent structure factor calculations. A further four cycles of anisotropic refinement, with the hydrogen atoms held in calculated[25] positions with $B = 6.0$ Å^2, led to convergence of refinement with $R_F = 0.071$, $R_{F^2} = 0.088$, $R_{wF^2} = 0.242$. The final suggested shifts in atomic parameters were each less than 6% of the appropriate standard deviation.

Throughout the analysis, scattering factors for neutral carbon, nitrogen, and hydrogen (as compiled by Ibers[26]) were used. The values for neutral sulfur[26a] and cobalt[26b] were corrected for the real part of the dispersion[26c] ($\Delta f'_{\text{Co}} = +0.4$ e^-, $\Delta f'_{\text{S}} = +0.1$ e^-) but not for the imaginary component ($\Delta f''_{\text{Co}} = +1.1$ e^-, $\Delta f''_{\text{S}} = +0.2$ e^-). The residual minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$.

Observed and calculated structure factors are shown in Table I. Atomic positions are collected in Table II. Anisotropic thermal parameters and their associated vibration ellipsoids are given in Tables III and IV, respectively.

TABLE II

FINAL POSITIONAL PARAMETERS (WITH ESD'S) FOR π-$C_5H_5CoS_2C_2(CN)_2$[a-c]

Atom	x	y	z
Co	0.09655 (6)	0.75163 (9)	0.15629 (7)
S_1	−0.0312 (1)	0.7770 (2)	0.0775 (2)
S_2	0.0856 (1)	0.5069 (2)	0.1776 (1)
N_1	−0.2256 (5)	0.5467 (12)	−0.0109 (7)
N_2	−0.0730 (5)	0.1877 (9)	0.1282 (6)
C_1	−0.0690 (4)	0.5907 (8)	0.0760 (5)
C_2	−0.0171 (5)	0.4715 (8)	0.1211 (6)
C_3	−0.1577 (5)	0.5618 (9)	0.0272 (5)
C_4	−0.0490 (5)	0.3125 (9)	0.1240 (5)
C_5	0.1272 (6)	0.9848 (10)	0.1743 (9)
C_6	0.1605 (6)	0.9111 (14)	0.1112 (6)
C_7	0.2154 (6)	0.7890 (13)	0.1636 (9)
C_8	0.2115 (6)	0.7946 (12)	0.2567 (7)
C_9	0.1546 (6)	0.9081 (11)	0.2616 (7)
H_5	0.0836	1.0822	0.1562
H_6	0.1492	0.9410	0.0370
H_7	0.2525	0.7106	0.1366
H_8	0.2457	0.7170	0.3146
H_9	0.1379	0.9372	0.3238

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. [b] Positions for hydrogen atoms are calculated assuming (i), a carbon–hydrogen bond distance of 1.080 Å and (ii) that hydrogen atoms are coplanar with the five π-cyclopentadienyl carbon atoms and are disposed such that the extension of each H–C bond bisects the pentagonal π-cyclopentadienyl system. [c] A hydrogen atom is numbered similarly to the carbon atom to which it is bonded.

The Molecular Structure

Interatomic distances are shown in Table V; bond angles are collected in Table VI.

This analysis shows that the ethene-1,2-dithiolate ligand in the π-$C_5H_5CoS_2C_2(CN)_2$ molecule bonds to the metal *via* sulfur–cobalt linkages only (this is also the case for π-$C_5H_5CoS_2C_2(CF_3)_2$[6]). The cobalt atom may be regarded as pentacoordinate since it is bonded to the bidentate dithiolate ligand and to a formally tridentate π-cyclopentadienyl system. The average cobalt–sulfur distance of 2.117 ± 0.003 Å would appear to be significantly greater than the value of 2.08 ± 0.01 Å reported for π-$C_5H_5CoS_2C_2(CF_3)_2$[6] but is lower than distances of 2.161 ± 0.002 Å in $[(n\text{-}C_4H_9)_4N]_2[Co\{S_2C_2(CN)_2\}]$[7] and 2.161 ± 0.016 Å in $Co_2[S_2C_2(CF_3)_2]_4$.[10] The S–Co–S angle of 93.2 ± 0.1° in the present complex is close to the 92.2° reported for π-$C_5H_5CoS_2C_2(CF_3)_2$.[6] Distances of the π-cyclopentadienyl carbon atoms from the cobalt range from 2.006 to 2.050 Å, averaging 2.029 Å. Variations from the mean are *not* statistically significant, but the average cobalt–carbon distance does seem to be lower than that observed in other π-cyclopentadienylcobalt complexes, *viz.*: 2.080 Å in π-$C_5H_5CoC_5H_5C_6H_5$,[27,28] 2.05 Å in π-$C_5H_5CoC_5H_5COC_6$-

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(21) Coefficients for the normal-sharpened Patterson synthesis were calculated using an updated version of PASHCO, an IBM 7090 program by B. R. Penfold.

(22) Patterson and Fourier syntheses were calculated using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090 by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende.

(23) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{F^2} = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$; $R_{wF^2} = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$.

(24) Structure factor calculations and least-squares refinement of positional and thermal parameters were peformed using ORFLS, a Fortran least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

(25) Hydrogen atoms were positioned such as to maintain the approximate D_{5h} symmetry of the ligand, with d(C–H) = 1.080 Å. These positions were not allowed to refine but were redefined (with respect to the new carbon atom positions) at the end of each cycle of refinement.

(26) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

(27) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 112 (1963).

(28) M. R. Churchill and R. Mason, *Proc. Roy Soc.* (London), **A279**, 191 (1964).

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR π-$C_5H_5CoS_2C_2(CN)_2$[a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	33.5 (0.7)	128.7 (2.6)	38.9 (0.9)	−6.4 (0.5)	11.9 (0.5)	−1.6 (0.6)
S_1	36.2 (1.0)	127.8 (3.1)	55.5 (1.4)	0.4 (1.2)	9.0 (0.8)	9.3 (1.4)
S_2	34.6 (1.0)	135.6 (3.6)	47.3 (1.3)	−1.4 (1.0)	10.2 (0.8)	9.8 (1.2)
N_1	37 (3)	344 (20)	71 (5)	−28 (7)	6 (4)	24 (8)
N_2	72 (4)	161 (13)	73 (5)	−41 (6)	26 (4)	9 (6)
C_1	26 (3)	133 (10)	47 (4)	4 (4)	12 (3)	5 (5)
C_2	33 (3)	153 (11)	53 (5)	−5 (5)	25 (3)	8 (6)
C_3	55 (5)	159 (13)	24 (4)	−4 (6)	8 (3)	24 (5)
C_4	34 (3)	177 (15)	40 (4)	−1 (5)	6 (3)	0 (6)
C_5	40 (4)	143 (14)	116 (10)	−0 (5)	15 (5)	14 (8)
C_6	67 (5)	286 (20)	52 (5)	−81 (9)	15 (4)	4 (9)
C_7	47 (5)	222 (15)	95 (8)	−41 (7)	26 (5)	−65 (10)
C_8	53 (4)	194 (14)	42 (4)	−29 (7)	−4 (3)	−20 (7)
C_9	53 (4)	208 (15)	58 (5)	−38 (7)	6 (4)	−17 (8)

[a] The anisotropic thermal parameter, T, is defined as: $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. [b] Esd's, in parentheses, are right-adjusted to the least significant digit of the preceding number.

TABLE IV

DIRECTION COSINES[a] FOR THE ATOMIC VIBRATION ELLIPSOIDS[b] IN π-$C_5H_5CoS_2C_2(CN)_2$

Atom	$B_{\max}$ (dc's major axis)	B_{med} (dc's median axis)	$B_{\min}$ (dc's minor axis)
Co	3.97 (−0.579, 0.809, 0.097)	3.24 (−0.811, 0.584, 0.243)	3.03 (−0.083, 0.065, 0.965)
S_1	5.05 (−0.597, 0.300, 0.900)	3.74 (0.687, 0.671, 0.035)	3.38 (0.415, −0.678, 0.430)
S_2	4.52 (−0.499, 0.652, 0.705)	3.61 (−0.814, −0.579, 0.223)	3.29 (0.297, −0.490, 0.673)
N_1	11.05 (−0.343, 0.900, 0.369)	5.63 (−0.362, −0.392, 0.918)	3.41 (0.867, 0.192, 0.145)
N_2	8.93 (−0.863, 0.503, 0.246)	5.82 (0.069, 0,205, 0.897)	3.03 (−0.500, −0.840, 0.367)
C_1	4.00 (0.042, 0.851, 0.479)	3.56 (−0.262, −0.495, 0.868)	2.61 (−0.964, 0.172, 0.131)
C_2	4.72 (0.193, 0.660, 0.620)	4.42 (0.474, −0.711, 0.332)	2.08 (−0.859, −0.244, 0.711)
C_3	6.40 (−0.917, 0.389, 0.385)	4.77 (0.393, 0.850, 0.200)	1.45 (−0.066, −0.355, 0.901)
C_4	5.12 (−0.042, 0.999, 0.029)	4.22 (−0.910, −0.045, 0.691)	2.85 (0.412, 0.003, 0.722)
C_5	9.76 (−0.332, −0.120, 0.993)	4.14 (−0.939, 0.132, 0.015)	4.03 (0.085, 0.984, 0.119)
C_6	12.54 (−0.669, 0.743, 0.239)	4.10 (0.077, 0.047, 0.913)	2.98 (−0.739, −0.667, 0.330)
C_7	10.10 (0.130, −0.659, 0.654)	5.27 (−0.806, 0.364, 0.708)	3.03 (0.577, 0.658, 0.264)
C_8	7.92 (−0.884, 0.414, 0.501)	5.78 (−0.264, −0.827, 0.557)	2.14 (0.386, 0.382, 0.663)
C_9	8.13 (−0.754, 0.653, 0.321)	5.70 (−0.398, 0.542, 0.830)	3.06 (0.523, 0.529, 0.456)

[a] Direction cosines are referred to the monoclinic axes. [b] Atomic vibration ellipsoids are presented in terms of the isotropic thermal parameter B. The transformation to root-mean-square displacement $(\bar{u}^2)^{1/2}$ is: $(\bar{u}^2)^{1/2} = [B/8\pi^2]^{1/2}$.

H_5,[29] 2.07 Å in π-$C_5H_5Co[(CH_3)_4C_5O]$,[30] and 2.075 Å in π-$C_5H_5Co[(CF_3)_4C_5O]$.[31] This presumably reflects the different electron-donating ability and/or π-acceptor capability of the dithiolate ligand *vis a vis* the conjugated cyclopentadiene or cyclopentadienone systems.

Carbon–carbon distances around the π-cyclopentadienyl ring range from 1.383 to 1.440 Å (each ±0.015 Å) and average 1.402 Å. The root-mean-square (rms) deviation from the least-squares plane through the five carbon atoms ($0.7034X + 0.6523Y + 0.2821Z = 7.0404$[32]) is 0.022 Å. Thus, the π-cyclopentadienyl ligand has D_{5h} symmetry within the limits of experimental error. The cobalt and the eight atoms of the 1,2-dicyanoethene-1,2-dithiolate ligand form a plane (rms deviation 0.025 Å) which has the equation $-0.4980X + 0.2104Y + 8412Z = 2.7386$.[32] Although there is no crystallographically imposed symmetry, the molecule possesses approximate C_s symmetry, the angle between π-cyclopentadienyl and $CoS_2C_2(CN)_2$ planes being 88.6°.

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(29) M. R. Churchill, *J. Organometal. Chem.* (Amsterdam), **4**, 258 (1965).

(30) L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **83**, 752 (1961).

(31) M. Gerloch and R. Mason, *Proc. Roy. Soc.* (London), **A279**, 170 (1964).

(32) (a) Planes were calculated using unit weights for all appropriate atoms; (b) planes are expressed in orthogonalized coordinates. These are related to the crystal axes by: $X = xa + zc\cos\beta$; $Y = yb$; $Z = zc\sin\beta$.

TABLE V

INTRAMOLECULAR DISTANCES FOR π-$C_5H_5CoS_2C_2(CN)_2$[a]

Atoms	Dist, Å	Atoms	Dist, Å
(a) Distances within the Dithiolate ligand			
Co–S_1	2.118 (3)	C_1–C_3	1.463 (11)
Co–S_2	2.116 (2)	C_2–C_4	1.462 (11)
S_1–C_1	1.707 (7)	C_3–N_1	1.114 (13)
S_2–C_2	1.697 (8)	C_4–N_2	1.146 (11)
C_1–C_2	1.364 (10)		
(b) Distances within the π-Cyclopentadienyl Ligand			
Co–C_5	2.043 (9)	C_5–C_6	1.395 (16)
Co–C_6	2.006 (12)	C_6–C_7	1.440 (16)
Co–C_7	2.028 (12)	C_7–C_8	1.406 (15)
Co–C_8	2.050 (10)	C_8–C_9	1.386 (14)
Co–C_9	2.020 (9)	C_9–C_5	1.383 (15)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least-significant digit in the preceding number. They have been calculated from the full correlation matrix using the IBM 7094 program ORFFE, a crystallographic function and error program by W. R. Busing and H. A. Levy.

TABLE VI

BOND ANGLES WITHIN THE π-$C_5H_5CoS_2C_2(CN)_2$ MOLECULE[a]

Atoms	Angle, deg	Atoms	Angle, deg
(a) Within the Dithiolate Ligand			
S_1–Co–S_2	93.2 (1)	C_2–C_1–C_3	120.8 (7)
Co–S_1–C_1	103.1 (2)	C_1–C_2–C_4	120.9 (7)
Co–S_2–C_2	103.3 (2)	C_1–C_3–N_1	176.9 (9)
S_1–C_1–C_2	120.1 (6)	C_2–C_4–N_2	178.6 (9)
S_2–C_2–C_1	120.3 (6)		
S_1–C_1–C_3	119.1 (5)		
S_2–C_2–C_4	118.8 (6)		
(b) Within the π-Cyclopentadienyl System			
C_5–Co–C_6	40.3 (5)	C_9–C_5–C_6	109.2 (9)
C_6–Co–C_7	41.8 (5)	C_5–C_6–C_7	107.4 (9)
C_7–Co–C_8	40.3 (4)	C_6–C_7–C_8	105.7 (9)
C_8–Co–C_9	39.8 (4)	C_7–C_8–C_9	109.6 (9)
C_9–Co–C_5	39.8 (4)	C_8–C_9–C_5	107.8 (9)

[a] See footnote *a* of Table V.

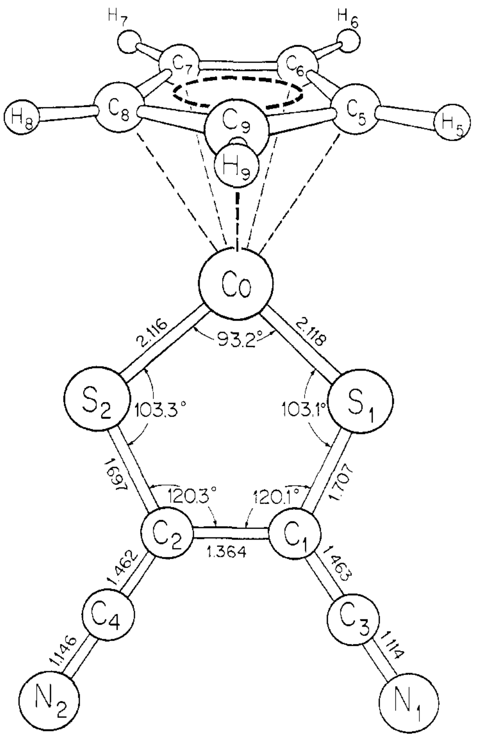

Figure 1.—Numbering of atoms and important dimensions in the π-$C_5H_5CoS_2C_2(CN)_2$ molecule.

TABLE VII

IMPORTANT DIMENSIONS WITHIN THE ETHENE-1,2-DITHIOLATE LIGANDS OF SOME TRANSITION METAL COMPLEXES

Complex	S—C, Å	C⩦C, Å	Ref
$V[S_2C_2(CN)_2]_3^{2-}$	1.72 ± 0.02	1.34 ± 0.03	16
$V[S_2C_2(C_6H_5)_2]_3$	1.69 ± 0.01	1.40 ± 0.02	14
$Mo[S_2C_2H_2]_3$	1.70 ± 0.03	1.34 ± 0.04	11
$Re[S_2C_2(C_6H_5)_3]_3$	1.69 ± 0.04[a]	1.34 ± 0.03	2
$Fe_2[S_2C_2(CN)_2]_4^{2-}$	1.73 ± 0.03	1.39 ± 0.03	15
$Co_2[S_2C_2(CF_3)_2]_4$	1.694 ± 0.016	1.393 ± 0.020	10
$Co[S_2C_2(CN)_2]_2^{2-}$	1.723 ± 0.007	1.34 ± 0.01	7
π-$C_5H_5CoS_2C_2(CF_3)_2$	1.74 ± 0.05	1.48 ± 0.05	6
π-$C_5H_5CoS_2C_2(CN)_2$	1.702 ± 0.007	1.364 ± 0.010	*b*
$Ni[S_2C_2(CN)_2]_2^{2-}$	1.75 ± 0.02	1.33 ± 0.02	9
$Ni[S_2C_2(CN)_2]_2^{-}$	1.714 ± 0.004	1.356 ± 0.007	12
$Ni[S_2C_2(C_6H_5)_2]_2$	1.71 ± 0.01	1.370 ± 0.014	13
$Cu[S_2C_2(CN)_2]_2^{-}$	1.72 ± 0.01	1.32 ± 0.02	8

[a] S–C varies from 1.62 to 1.75 Å. [b] This work.

The 1,2-Dicyanoethene-1,2-dithiolate Ligand.—Figure 1 shows the essential geometry of the dithiolate ligand. The mean carbon–sulfur bond length (1.702 ± 0.007 Å) is in good agreement with that found in other dithiolate complexes (see Table VII). Although this distance is demonstrably shorter than the value of 1.817 ± 0.005 Å recognized for a C—S single bond and is close to the value of 1.71 ± 0.01 Å found for C═S,[33] Fritchie[12] has pointed out that the rehybridization involved in bonding a sulfur atom to a metal may result in the covalent radius changing by an uncertain amount. Thus it can be said only that our present value of C—S = 1.702 ± 0.007 Å is consistent with *some* multiple bond character. Rather more information is forthcoming from the carbon–carbon distance within the "ethene" residue. The C_1—C_2 bond distance of 1.364 ± 0.010 Å corresponds to a bond order of ~1.7.[34] It seems, therefore, that there is some delocalization of charge within the dithiolate moiety but that a valence-bond description would involve a greater contribution from the ethylene-1,2-dithiolate resonance form (IV) than from the ethane-1,2-dithione structure (III). [It should be noted that Baird and White's value of 1.48 ± 0.05 Å for the C_1—C_2 distance in π-$C_5H_5CoS_2C_2(CF_3)_2$, which constitutes their main evidence for a dithioketone structure, is not significantly different from our value at the 2.4σ level.]

The geometry of the dithiolate ligand in the present complex is indistinguishable from that of the corresponding ligand in the simple bis-square-planar complexes that have been examined.[7–9,12,13] It appears that the distances within a dithiolate system (except possibly, the peripheral metal–sulfur distances) are not particularly dependent on the coordination stereochemistry of the metal. Furthermore, from the available data it would appear that dimensions within di-

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(33) Reference 17, p S22s.

(34) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 237.

TABLE VIII

INTERMOLECULAR CONTACTS (TO 3.5 Å) WITHIN THE π-$C_5H_5CoS_2C_2(CN)_2$ CRYSTAL

Atom	Atom[a]	Dist, Å	Atom	Atom[a]	Dist, Å
S_1	H_9(II)	3.01	H_5	N_2(IV)	2.72
S_1	H_6(XIII)	3.22	H_5	C_4(IV)	2.91
S_1	H_5(XIII)	3.49	H_5	H_8(III)	3.02
N_1	H_6(XI)	2.62	H_5	N_2(VII)	3.38
N_1	H_9(XII)	2.76	H_5	S_1(XIII)	3.49
N_1	H_7(VI)	2.81	H_6	N_2(VI)	2.60
N_1	H_8(XII)	3.18	H_6	N_1(I)	2.62
N_1	C_6(XI)	3.27	H_6	S_1(XIII)	3.22
N_1	C_9(XII)	3.33	H_6	C_4(VI)	3.25
N_1	H_8(II)	3.37	H_6	H_9(XIV)	3.27
N_2	H_6(VI)	2.60	H_6	H_8(III)	3.30
N_2	H_9(VIII)	2.61	H_6	C_3(I)	3.50
N_2	H_5(V)	2.72	H_7	N_1(VI)	2.81
N_2	H_7(XI)	3.03	H_7	H_9(IX)	2.92
N_2	H_5(VIII)	3.38	H_7	N_2(I)	3.03
N_2	C_9(VIII)	3.43	H_7	C_9(IX)	3.13
N_2	C_6(VI)	3.46	H_7	C_3(VI)	3.35
C_3	H_7(VI)	3.35	H_7	C_5(IX)	3.45
C_3	H_8(II)	3.44	H_8	C_5(IX)	2.90
C_3	H_6(XI)	3.50	H_8	H_5(IX)	3.02
C_4	H_5(V)	2.91	H_8	C_6(IX)	3.06
C_4	H_6(VI)	3.25	H_8	N_1(X)	3.18
C_5	H_8(III)	2.90	H_8	H_6(IX)	3.30
C_5	H_7(III)	3.45	H_8	N_1(II)	3.37
C_6	H_8(III)	3.06	H_8	C_3(II)	3.44
C_6	N_1(I)	3.27	H_9	N_2(VII)	2.60
C_6	N_2(VI)	3.46	H_9	N_1(X)	2.76
C_9	H_7(III)	3.13	H_9	H_7(III)	2.92
C_9	N_1(X)	3.33	H_9	S_1(II)	3.01
C_9	N_2(VII)	3.43	H_9	H_6(XV)	3.27

[a] Transformations are: (I) $^1/_2 + x, ^1/_2 + y, z$; (II) $-x, y, ^1/_2 - z$; (III) $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$; (IV) $x, 1 + y, z$; (V) $x, -1 + y, z$; (VI) $-x, 1 - y, -z$; (VII), $-x, 1 + y, ^1/_2 - z$; (VIII) $-x, -1 + y, ^1/_2 - z$; (IX) $^1/_2 - x, -^1/_2 + y, ^1/_2 - z$; (X) $^1/_2 + x, ^3/_2 - y, ^1/_2 + z$; (XI) $-^1/_2 + x, ^1/_2 + y, z$; (XII) $-^1/_2 + x, ^3/_2 - y, -^1/_2 + z$; (XIII) $-x, 2 - y, -z$; (XIV) $x, 2 - y, -^1/_2 + z$; (XV) $x, 2 - y, ^1/_2 + z$.

thiolate ligands are not strongly dependent upon the nature of the substituent R (R = H, CN, CF_3, C_6H_5 in $S_2C_2R_2$) although they may be a function of the formal charge on the complex ion.[13]

Crystal Packing.—Molecules in the π-$C_5H_5CoS_2C_2(CN)_2$ lattice are separated by normal van der Waals forces. Table VIII includes all intermolecular contacts to 3.5 Å. Figures 2 and 3 show the unit cell viewed down *b* and *c*, respectively. The structure consists of pillars of $CoS_2C_2(CN)_2$ groups which are surrounded by π-cyclopentadienyl ligands. The projection of the structure down *c* shows mm symmetry and is rather similar to that of $[N(n\text{-}C_4H_9)_4]\{Cu[S_2C_2(CN)_2]\}$.[8]

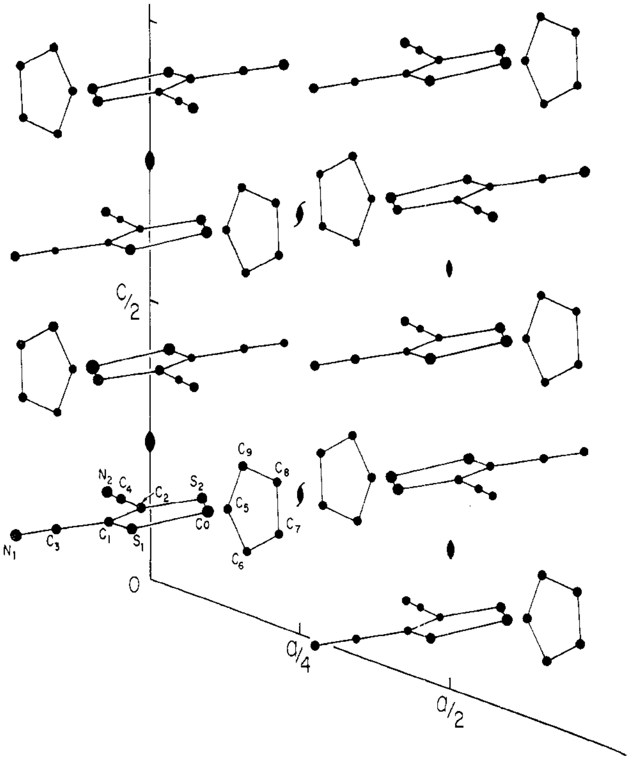

Figure 2.—Packing diagram for π-$C_5H_5CoS_2C_2(CN)_2$, viewed down *b*.

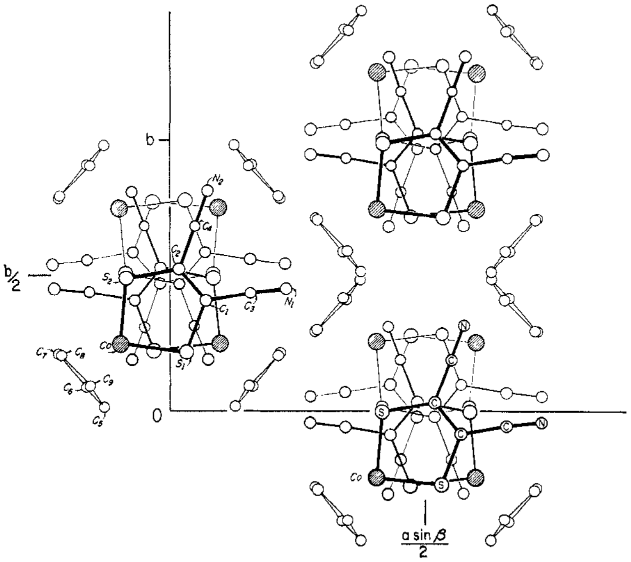

Figure 3.—Packing diagram for π-$C_5H_5CoS_2C_2(CN)_2$, viewed down *c*.

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