comparable spectroscopic comparison is encountered with the $M_2(O_2C\text{-aryl})_4$ molecules of molybdenum and tungsten and will be discussed in detail in a forthcoming publication.[21]

Because the $M_2(\text{fhp})_4$ molecules have polar character with C_{4v} effective symmetry, the M–M stretching vibration is formally active in the infrared spectrum. The frequency of such a band is not subject to much uncertainty. From the bond length, and by comparison to a number of other quadruply bonded dimolybdenum compounds in which $\nu_{\text{Mo-Mo}}$ is known,[22] a frequency of about 425 cm^{-1} would be expected. The only question is whether the vibration will have enough intensity in the infrared region to be observed. We first measured the infrared spectrum of a THF solution of $Mo_2(\text{fhp})_4(\text{THF})$, obtaining the result shown in Figure 4. The strong band at 430 cm^{-1} seemed a reasonable candidate for assignment to the Mo–Mo stretching mode. In an attempt to get supporting evidence, the Raman spectrum was also recorded, but it showed no strong lines in the entire 280–760-cm^{-1} region, and none of the three medium to weak lines at 370, 405, and 643 cm^{-1} matches the 430-cm^{-1} band in the infrared spectrum. Strong lines were recorded at 280 and 760 cm^{-1} and at higher frequencies where ligand-localized vibrations would be expected. We have encountered this problem before with all other $M_2(\text{Xhp})_4$ ligands except the $M_2(\text{mhp})_4$ compounds. No reason for the absence of an intense $\nu_{\text{M-M}}$ band in these cases has ever been found, but empirically, the present case is in no sense exceptional. As an alternative way of testing the assignment of the 430-cm^{-1} band, the infrared spectrum of the $W_2(\text{fhp})_4(\text{THF})$ compound was recorded; this too is shown in Figure 4.

Comparison of the two spectra does not lead unambiguously to a decision, but it does provide qualified support for assigning the 430-cm^{-1} band of $Mo_2(\text{fhp})_4(\text{THF})$ to the Mo–Mo stretching mode. If the absorption bands seen in the $W_2(\text{fhp})_4(\text{THF})$ spectrum at ca. 390, 440, and 470 cm^{-1} were reduced in intensity to match absorptions at about those frequencies in $Mo_2(\text{fhp})_4(\text{THF})$ (i.e., by a factor of 3–4) it would be clear that the $W_2(\text{fhp})_4(\text{THF})$ spectrum contains no band comparable in position and relative intensity to the 430-cm^{-1} band of $Mo_2(\text{fhp})_4(\text{THF})$. The change from Mo_2 to W_2 should have as its major effect the shifting of the M–M stretching band from 430 cm^{-1} to a frequency below 300 cm^{-1} (where there is, unfortunately, strong absorption by THF and/or the ligands). We thus think it likely that in this very polar situation the $\nu_{\text{Mo-Mo}}$ mode of $Mo_2(\text{fhp})_4(\text{THF})$ is being observed in the infrared spectrum.

Acknowledgment. We are grateful to the National Science Foundation for financial support and to Dr. Charles Angell for running the Raman spectrum.

Registry No. $Cr_2(\text{fhp})_4(\text{THF})\cdot\text{THF}$, 87739-04-6; $Mo_2(\text{fhp})_4(\text{THF})$, 87761-48-6; $W_2(\text{fhp})_4(\text{THF})$, 87739-05-7; $Mo_2(\text{mhp})_4$, 67634-80-4; $W_2(\text{mhp})_4$, 67634-84-8; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8; WCl_4, 13470-13-8; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Tables of temperature factor expressions, bond distances and angles, thermal vibration amplitudes, positional parameters, and observed and calculated structure factors for each compound (76 pages). Ordering information is given on any current masthead page.

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(22) Reference 1, Table 8.5.1.

Contribution from Bell Laboratories,
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The Chemistry of the 1,2-Dicyanocyclopentadienide Anion: Metal Complexes and Nucleophilic Substitution Reactions

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Reactions of the 1,2-dicyanocyclopentadienide (DCCP) anion with various metal salts have been explored. Stable complexes with silver(I), copper(I), manganese(II), and cobalt(II) have been prepared and analyzed. The crystal structure of the cobalt(II) complex is reported. It crystallizes in the centrosymmetric orthorhombic space group *Pnna*, with cell dimensions $a = 28.538$ (9) Å, $b = 14.044$ (4) Å, $c = 9.017$ (2) Å, $V = 3614$ (2) Å^3, and $Z = 4$. Diffraction data were collected with a Syntex P$\bar{1}$ diffractometer using Mo Kα radiation of $\lambda = 0.71069$ Å, and the structure was refined to $R = 0.087$ for 1448 independent reflections. The compound takes the form of a unique cobalt polymer with repeating units defined as $Co[C_5H_3(CN)_2]_4[N(CH_3)_4]_2$. The reaction of the DCCP anion with the 2-(methylthio)-1,3-dithiolium cation results in the formation of the heterosesquifulvalene 2-(3,4-dicyanocyclopentadienylidene)-1,3-dithiole. NMR spectral data imply a large contribution of the dipolar form to the electronic structure of this compound.

Introduction

Donor molecules based on tetrathiafulvalene (TTF)[1,2] have long been the staple of solid-state chemists interested in new low-dimensional organic electrical conductors.[3] Many of the first conducting solids were combinations of TTF analogues and tetracyano-*p*-quinodimethane (TCNQ).[4,5]

The acceptor properties of TCNQ,[6] and cyano-based acceptor molecules in general,[7] are important for the successful

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(2) General reference on properties: Kaplan, M. L.; Wudl, F.; Haddon, R. C.; Hauser, J. J. *Chem. Scr.* **1980**, *15*, 196.

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(6) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.

preparation of interesting donor–acceptor (DA) materials. In connection with research directed toward the preparation of new acceptors, attempts were made to study the oxidative coupling reactions and nucleophilic substitution reactions of the 1,2-dicyanocyclopentadienide (DCCP) anions.[8] Similarly, Smith and West[9] prepared the electron-deficient cyclopentadiene-based acceptor octachlorofulvalene (I) to examine its properties.

In our own work several transition-metal-mediated oxidations were attempted, with unexpected products obtained in some cases. In particular, the coupling of DCCP attempted with Co^{2+} resulted in a most unusual product, which was characterized by IR and optical spectroscopy and ultimately by a single-crystal X-ray diffraction study. We report here the results of synthetic efforts to oxidatively couple the DCCP anion and the crystal and molecular structure of the *product* of the reaction of the tetramethylammonium salt of the DCCP anion with $CoCl_2$, a *novel* octahedral Co(II) complex. Also, in the course of our studies we attempted to determine the relative ease of electrophilic attack on the available sites in the DCCP anion. A new, stable heterosesquifulvalene was obtained. Its properties are also reported.

Experimental Section

Silver(I) Dicyanocyclopentadienide. A solution of (TMA)(DCCP)[8] (945 mg, 5 mmol) in 25 mL of CH_3CN was mixed with a solution of $AgNO_3$ (850 mg, 5 mmol) in 25 mL of CH_3CN. An immediate white crystalline precipitate formed, which was collected after the mixture was refrigerated overnight: yield quantitative; mp >150 °C dec. Anal. Calcd for $C_7H_3N_2Ag$: C, 37.71; H, 1.36; N, 12.56. Found: C, 37.34; H, 1.22; N, 12.47. IR (KBr): CN 2250 cm^{-1}.

Copper(I) Complex of DCCP. Solutions of CuI (952 mg, 5 mmol) and (TMA)(DCCP) (945 mg, 5 mmol) in acetonitrile were mixed (total volume 50 mL). After storage of the mixture for 5 days at −30 °C, the tan solid that had formed was collected: yield 0.73 g (31% based on CuI); mp 213–215 °C dec. Anal. Calcd for $C_{33}H_{47}N_9Cu_2I_2O$: C, 41.00; H, 4.90; N, 13.0. Found: C, 40.82; H, 5.23; N, 12.53. IR (KBr): CN 2200 cm^{-1}, H_2O 3500 cm^{-1}.

Manganese(II) Complex of DCCP. Homogeneous aqueous solutions of $MnCl_2 \cdot 4H_2O$ (495 mg, 2.5 mmol) and (TMA)(DCCP) (945 mg, 5 mmol) were mixed. An immediate tan precipitate formed and was collected after the mixture was refrigerated for ~16 h: yield 0.52 g (39% based on $MnCl_2 \cdot 4H_2O$); mp >220 °C dec. A small portion was recrystallized from acetonitrile for elemental analysis. Anal. Calcd for $C_{54}H_{50}N_{16}Mn_2O$: C, 61.83; H, 4.80; N, 21.36. Found: C, 62.11; H, 4.35; N, 21.21.

Cobalt(II) Adduct of DCCP. A solution of $CoCl_2 \cdot 6H_2O$ (1.190 g, 5 mmol) in 50 mL of CH_3CN was mixed with a solution of (TMA)(DCCP) (1.890 g, 10 mmol) in 25 mL of CH_3CN. The original deep blue solution became deep green. When it was cooled to −78 °C, an aqua powder separated (appears to be wholly inorganic), which was removed by filtration. Diethyl ether was added to the filtrate and a fine chartreuse solid separated and was collected and washed with ether: yield 1.88 g; mp 225–226 °C, with decomposition and NH_3 evolution. IR (KBr): CN 2200 cm^{-1}. The attempted recrystallization of this material from CH_3CN resulted in conversion of the chartreuse powder to reddish orange hexagonal crystals; dec pt >250 °C. IR (KBr): CN 2200 cm^{-1}. The band at 725 cm^{-1} is absent in the chartreuse compound. All other IR bands are identical. The crystal and molecular structures of this compound are reported here.

2-(Methylthio)-1,3-dithiolium Hexafluorophosphate. To an aqueous slurry (~50 mL of H_2O) of 2-methylthio-1,3-dithiolium iodide[10] (2.76 g, 0.01 mol) was added $NaPF_6$ (3.36 g, 0.02 mol). The mixture was stirred at room temperature for 30 min and then filtered. The solid was air-dried; yield 2.58 g (88%). Recrystallization of the solid from 1,2-dichloroethane afforded colorless needles, mp >190 °C dec. Anal. Calcd for $C_4H_5S_3PF_6$: C, 16.33; H, 1.71. Found: C, 16.09; H, 1.86. NMR (Me_4Si, CD_3CN): singlets at δ 3.11 (3 H) and 8.5 (2 H).

Table I. Physical Data and Data Collection Parameters

mol formula (repeating unit)	$C_{36}N_{10}H_{36}Co$
mol wt	667.3
crystal size, mm	0.18 × 0.22 × 0.18
cell dimens	
a, Å	28.538 (9)
b, Å	14.044 (4)
c, Å	9.017 (2)
V, Å^3	3614 (2)
space group	*Pnna*
molecules/unit cell	4
d(calcd), g/cm^3	1.23
d(obsd),^{a} g/cm^3	1.25
scan technique	$\theta/2\theta$
scan speed	2°/min in 2θ
scan width	1.2° below $K\alpha_1$ to 1.2° above $K\alpha_2$
bkgd count time	0.6 × scan time on each side of peak
no. of reflctns	2354
no. of nonzero reflctns^b	1448

^{a} Density was measured by the flotation technique using hexane/1,3-dibromopropane. ^{b} All intensities with values less than 3 × standard deviation were set equal to zero with zero weight.

2-(3,4-Dicyanocyclopentadienylidene)-1,3-dithiole (VI). A solution of (TMA)(DCCP) (0.095 g, 5×10^{-4} mol) in 10 mL of CH_3CN was mixed with a solution of 2-(methylthio)-1,3-dithiolium hexafluorophosphate (0.147 g, 5×10^{-4} mol) in 10 mL of CH_3CN. An immediate orange solution formed, which deposited orange needles. The solid was collected, washed successively with CH_3CN and diethyl ether, and then air-dried: yield 0.056 g (52%); mp >290 °C dec. NMR (Me_2SO-d_6, Me_4Si): singlets at δ 7.17 and 8.05. Anal. Calcd for $C_{10}H_4S_2N_2$: C, 55.53; H, 1.86; N, 12.95. Found: C, 55.68; H, 1.76; N, 13.32.

Crystal Data Collection. Orange, spherically shaped crystals of the cobalt complex of DCCP suitable for an X-ray analysis were grown by the slow evaporation of an acetonitrile solution. The crystal survey, unit cell dimension determination, and data collection were accomplished on a Syntex P$\bar{1}$ diffractometer using molybdenum radiation (λ = 0.71069 Å) at room temperature. The diffractometer was equipped with a graphite incident-beam monochromator mounted in the perpendicular mode. Final unit cell dimensions were obtained by a least-squares fit of 15 high-angle reflections ($2\theta > 15°$). Systematic absences indicated that the crystal belonged to the centrosymmetric orthorhombic space group *Pnna* ($0kl$, $k + l = 2n + 1$; $h0l$, $h + l = 2n + 1$; $hk0$, $h = 2n + 1$). A 1-Å intensity data set was collected (maximum $(\sin \theta)/\lambda = 0.5$). One check reflection monitored every 30 reflections revealed no unexpected variation in intensity. Details of the crystal survey and data collection parameters are summarized in Table I.

The diffractometer output and all subsequent crystallographic calculations were processed by using subprograms of the CRYM crystallographic computer system.[11] The data processing included corrections for background, Lorentz, and polarization effects. Polarization due to the monochromator was corrected for by a method suggested by Azaroff.[12] Processing also included the calculation of F^2 and its standard deviation for each reflection. The standard deviations were assigned on the basis of the equations $\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$, where S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0.02, and α is the scan time to total background time ratio. As a result of the "equidimensional" nature of the crystal and the low linear absorption coefficient (μ = 5.4 cm^{-1}), no absorption corrections were made.

Finally, the data set was placed on an approximately absolute scale by Wilson statistics.[13] Atomic scattering factors for C and N were taken from ref 14, for Co^{2+} from Cromer and Mann,[15] and for H from

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Table II. Non-Hydrogen Atom Coordinates ($\times 10^4$) and Their Standard Deviations

	x/a	y/b	z/c
C01	7392 (1)	7500 (0)	7500 (0)
C2	8702 (4)	5687 (7)	8486 (12)
C3	8758 (4)	4694 (7)	8494 (12)
C4	9462 (4)	5394 (10)	8660 (14)
C5	8291 (4)	6164 (8)	8401 (13)
N6	7948 (4)	6605 (6)	8315 (10)
N7	8131 (3)	3438 (6)	8266 (10)
C8	9236 (4)	4518 (8)	8587 (13)
C9	8418 (4)	4007 (8)	8372 (12)
C10	9122 (4)	6120 (8)	8591 (13)
N11	5059 (5)	2315 (11)	9956 (16)
C12	4725 (6)	2395 (10)	9218 (18)
C13	4308 (5)	2475 (12)	8279 (14)
C14	3848 (4)	2450 (12)	8735 (20)
C15	3574 (7)	2500 (0)	7500 (0)
C16	7500 (0)	5000 (0)	986 (16)
C17	7532 (5)	4202 (7)	1906 (11)
C18	7519 (4)	4499 (6)	3374 (10)
N19	7587 (4)	3359 (6)	5546 (9)
C20	7564 (4)	3892 (7)	4576 (12)
C21	8933 (15)	5054 (19)	4912 (24)
C22	8824 (7)	6438 (12)	3914 (28)
C23	8738 (5)	4948 (11)	2502 (20)
C24	9428 (8)	5427 (24)	3422 (35)
N25	8999 (4)	5539 (8)	3524 (13)

Stewart, Davidson, and Simpson.[16] The scattering factor for Co(II) was corrected for the real anomalous scattering component.[15]

Determination and Refinement of Structure. The position of the cobalt atom was determined from the direct-methods program package MULTAN.[17] Subsequent difference Fourier maps allowed the location of all carbon and nitrogen atoms. The cobalt atom was found to occupy a special position on a 2-fold rotation axis. In the space group *Pnna*, this special position was $\bar{x}$, $^3/_4$, $^3/_4$. Other unique atoms in the asymmetric unit were one bridging DCCP unit, half of another bridging DCCP unit, half of a nonbonded "outer-sphere" DCCP unit, and one TMA molecule. Both DCCP units mentioned above were also located on 2-fold rotation axes. The other "halves" of the ring systems were generated by application of the appropriate rotation axis. This trial structure refined routinely to an acceptable R index of 0.087.

The refinement was concluded by using a full-matrix least-squares technique. The quantity minimized by the least-squares procedure was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Hydrogen positions were calculated whenever required. While the hydrogen parameters were added to the structure factor calculations during the later stages of refinement, they were not refined. During the final cycles of refinement of the scale factor, non-hydrogen coordinates and non-hydrogen anisotropic temperature factors were located in a single matrix. Refinement of a secondary extinction coefficient proved that this correction was insignificant. During the final stages of refinement, when numerous models for the disorder of the cations were being tested, the geometry of the Co(DCCP) unit was not significantly altered. Disorder in the cations was examined after the temperature factors were refined in an anisotropic manner. Difference Fourier maps revealed that there were no plausible multiple occupancy models that would better fit the data and that thermal ellipsoids were the best (although not perfect) way to fit the data. In addition, crystals were grown at 0 °C to help remove the problem of disorder. Unfortunately, these crystals showed the same disorder. A data collection at reduced temperature was not tried because while this would have reduced the thermal parameters, it would not have eliminated the disorder problem. This disorder in the cations seems to be a common occurrence and has been reported by other workers.[18,19] The somewhat high data-fit criteria values may be attributed to the high thermal motion of the cations. The refinement was terminated when the shifts calculated for the parameters in the least-squares cycles were all zero. A final difference Fourier map revealed no additional extraneous electron density. The data-fit criteria (based on nonzero reflections) were

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.087$$

$$R' = \sum w(F_o^2 - F_c^2)^2 / \sum F_o^4 = 0.030$$

$$\mathrm{GOF} = [\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2} = 4.21$$

The refined coordinates were plotted with use of the ORTEP computer program of Johnson[20] (Figure 1). The final non-hydrogen atom coordinates are given in Table II; thermal parameters are presented

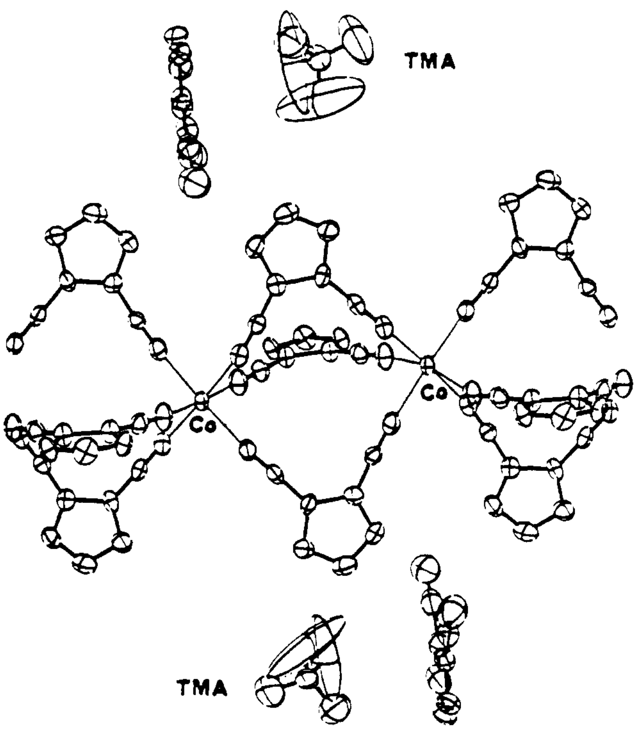

Figure 1. ORTEP plot of the solid-state structure of Co(DCCP)$_4$(TMA)$_2$. For purposes of clarity, two TMA cations associated with the cobalt atoms were omitted.

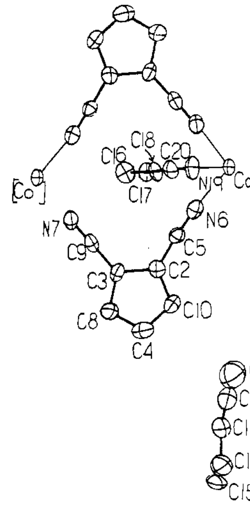

Figure 2. Pictorial representation of the numbering system used for labeling each unique atom in Co(DCCP)$_4$(TMA)$_2$ (note: TMA cation not shown; hydrogens omitted for clarity).

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in Table III (supplementary material). Figure 2 indicates the numbering system for the unique atoms.

Results and Discussion

Metal Complexes of Dicyanocyclopentadienide Anion. When equimolar amounts of tetramethylammonium (TMA) dicyanocyclopentadienide[8] and silver nitrate were mixed in CH_3CN solution, a white, crystalline solid was formed. Elemental analysis and spectroscopic examination of this substance gave results consistent with the formation of Ag^IDCCP. The NMR spectrum, in Me_2SO-d_6, exhibited the characteristic DCCP anion pattern consisting of a triplet at δ 5.55 and a doublet at δ 6.05. The nitrile IR absorption of the Ag^IDCCP occurs at 2250 cm^{-1} (in KBr), which is slightly shifted from the $(CH_3)_4N^+DCCP^-$ absorption at 2180 cm^{-1}.

When a similar reaction was tried with anhydrous CuI in CH_3CN, a tan solid separated upon cooling. The solid melted at 213–215 °C with decomposition. This time, however, elemental analysis did not provide a simple formulation. An acceptable stoichiometry for the data is $[DCCP]_3[TMA]_3[H_2O][CuI]_2$.

The most interesting results in this series were obtained when $MnCl_2$ and $CoCl_2$ were reacted with (TMA)(DCCP). In the case of the former, the reaction was carried out in aqueous solution, and the product gave an analysis that was best fit by $Mn_2[DCCP]_3[TMA]_2[CH_3CN]_2[H_2O]$. The NMR spectrum in CD_3CN showed only the absorption due to TMA (broad line). The lines due to the DCCP were not visible, probably due to broadening by spin–lattice relaxation effects. The reaction of (TMA)(DCCP) with $CoCl_2$ was carried out in CH_3CN and gave a chartreuse solid. Elemental analyses were not definitive. However, the best formulation to fit the data was $Co_2[DCCP]_3[TMA]_2Cl_3[H_2O]_2$. It was unclear at this stage whether or not a mixture of two or more components was present. Fractional crystallization from acetonitrile was attempted. During the process, a startling change occurred. Upon warming, all of the chartreuse product dissolved, the solution color changed from green to orange, and red-orange hexagonal crystals deposited. The nitrile IR absorption of this material occurred at 2200 cm^{-1} (in KBr). The UV–vis spectrum revealed an absorption at 410 nm characteristic of a high-spin octahedral Co^{2+} center. The crystal and molecular structure of this material was determined and is discussed below. Green crystals that were obtained in a later fraction are devoid of any CN stretches, indicating either that this is a two-component system or that some chemical transformation had occurred. Attempts to grow suitable crystals of this second component are in progress.

Description of Structure. The molecular structure of the Co(II) complex of DCCP consists of repeating units of $Co(DCCP)_4(TMA)_2$ forming a polymeric compound. It has been recognized that transition-metal complexes of percyanocarbons may be polymeric in nature.[21] For example, Fe, Co, Ni, Cu, and Mn complexes of the tricyanomethanide (TCM) anion, on the basis of spectral and magnetic measurements, were proposed to be polymeric.[22] An X-ray study of the copper compound showed this proposal to be correct.[23] In addition, polymeric structures have been suggested for TCM–transition-metal complexes containing amine ligands[24,25] or Me_2SO.[26] The data for all the above polymeric complexes are consistent with materials possessing octahedral coordination around the metal (in the solid state).

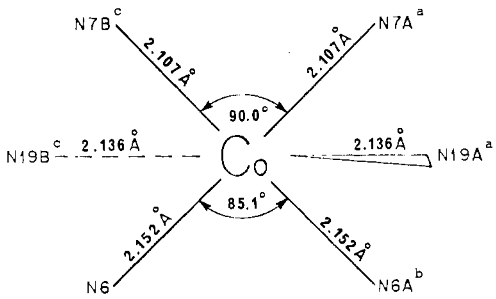

Figure 3. Schematic drawing of the inner coordination of the cobalt atoms in $Co(DCCP)_4(TMA)_2$: (a) N7A and N19A generated by symmetry operation $\bar{x} + 1.5$, $y - 0.5$, $\bar{z} + 1.5$; (b) N6A generated by symmetry operation x, $\bar{y} + 1.5$, $\bar{z} + 1.5$; (c) N7B and N19B generated by symmetry operation $\bar{x} + 1.5$, $\bar{y} + 1.0$, z.

Table IV. Distances (Å) and Angles (deg) within the Coordination Sphere

	Distances		
Co–N6	2.152 (4)	Co–N7A	2.107 (4)
Co–N19A	2.136 (4)		
	Trans Angles		
N19B[c]–Co–N19A[a]	176.8 (3)	N6A[b]–Co–N7B[c]	177.0 (4)
N6–Co–N7A[a]	177.0 (4)		
	Cis Angles		
N7A–Co–N7B	89.9 (4)	N7A–Co–N19A	86.4 (3)
N6A–Co–N7A	92.5 (2)	N6–Co–N19A	91.6 (3)
N6–Co–N6A	85.1 (4)	N7A–Co–N19B	95.9 (3)
N6–Co–N7B	92.5 (2)		

[a] N7A and N19A generated by symmetry operation $x - 1.5$, $\bar{y} + 0.5$, $z - 1.5$. [b] N6A generated by symmetry operation $\bar{x}$, $y - 1.5$, $z - 1.5$. [c] N7B and N19B generated by symmetry operation $x - 1.5$, $y - 1.0$, $\bar{z}$.

Polymeric chelates formed from transition metals and tetracyanoethylene (TCNE) have also been reported.[27,28]

In our case, each Co atom formally in the +2 oxidation state is bound to six nitrogen atoms, derived from the cyano groups of the DCCP anions, in an octahedral environment. Figure 3 shows a schematic drawing of the details of the inner coordination sphere. Each *bound* DCCP unit is bridging in nature and therefore may be formally considered a bidentate ligand. In addition to the liganded bridging DCCP units, there is also an "outer-sphere" DCCP anion with a complementary TMA cation nearby. With the oxidation state of the cobalt +2, each cobalt atom is associated with three *full* DCCP units, each of which is formally 1− in terms of charge. In order to maintain electroneutrality, associated with each cobalt atom is a TMA cation. Thus, the net charge on the repeating unit is zero.

The C≡N distances of the bound DCCP units range from 1.153 (13) to 1.148 (14) to 1.163 (15) Å, while the C≡N distance of the outer-sphere DCCP unit is 1.167 (21) Å (see Table V). It may then be argued with some certainty that all distances are within 1.0σ of one another, and therefore retrodative π-back-bonding interactions between the Co atom and the C≡N groups are insignificant. In addition, the in-plane or basal Co–N distances are 2.107 (4) and 2.152 (4) Å, while the axial Co–N distances are 2.136 (4) Å. The near equivalence of the basal and axial distances supports the concept of a high-spin Co(II) center. If a low-spin Co(II) center were the case here, one would expect at least a 0.10 Å difference in terms of bond length between the basal and axial Co–N distances, as well as a general *decrease* in the actual values of 2.107–2.152 Å.

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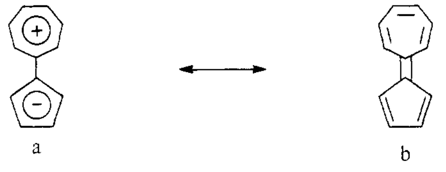
Table V. Distances (Å) and Angles (deg) outside the Coordination Sphere

C2-C3	1.405 (14)	C13-C14	1.375 (18)
C2-C5	1.351 (15)	C14-C15	1.363 (19)
C2-C10	1.347 (15)	C16-C17	1.398 (13)
C3-C8	1.388 (15)	C17-C18	1.388 (13)
C3-C9	1.373 (15)	C18-C20	1.385 (14)
C4-C8	1.391 (17)	N19-C20	1.153 (13)
C4-C10	1.410 (17)	C21-N25	1.437 (26)
C5-N6	1.163 (15)	C22-N25	1.402 (21)
N7-C9	1.148 (14)	C23-N25	1.446 (20)
N11-C12	1.167 (21)	C24-N25	1.239 (26)
C12-C13	1.466 (20)		
C5-C2-C3	126.3 (10)	C14-C13-C12	126.9 (13)
C10-C2-C3	110.2 (9)	C15-C14-C13	107.6 (14)
C10-C2-C5	123.4 (10)	C18-C17-C16	108.9 (9)
C8-C3-C2	106.8 (9)	C20-C18-C17	124.0 (9)
C9-C3-C2	128.0 (10)	N19-C20-C18	176.9 (11)
C9-C3-C8	125.1 (10)	C22-N25-C21	99.3 (17)
C10-C4-C8	108.5 (10)	C23-N25-C21	102.4 (16)
N6-C5-C2	177.5 (12)	C24-N25-C21	97.7 (23)
C4-C8-C3	107.6 (10)	C23-N25-C22	119.5 (13)
N7-C9-C3	179.4 (12)	C24-N25-C22	119.0 (19)
C4-C10-C2	106.9 (10)	C24-N25-C23	112.9 (18)
C13-C12-N11	178.8 (16)		

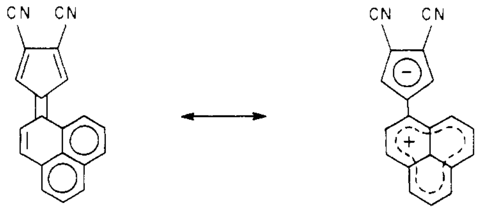
The inner coordination sphere distances and angles are given in Table IV. The "trans" angles are 176.8 (3) and 177.0 (4)°, while the "cis" angles range from 85.1 (4) to 95.9 (3)°. The Co—N≡C angles, surprisingly, are significantly distorted from linearity. These angles range from 162.8 (3) to 165.5 (3)° and are probably a result of the strain associated with the bridging nature of the entire polymer unit. In terms of the crystallographic asymmetric unit, the entire in-plane μ-DCCP ring was found to be unique, while the out-of-plane (x plane by definition) μ-DCCP ring was located on a 2-fold rotation axis. In addition, the "outer-sphere", nonbonded DCCP ring was also located on a C_2 axis and the other "halves" of each ring system were generated by application of the appropriate symmetry operation. For purposes of clarity, the two TMA cations associated with the two cobalt atoms were omitted in the ORTEP drawing (Figure 1).

2-(3,4-Dicyanocyclopentadienylidene)-1,3-dithiole. A Heterosesquifulvalene. In a further attempt to couple the DCCP anion through the 4-position (3-position relative to the cyano group), and to ascertain whether this was the sole site for electrophilic attack, we chose for our experiments an electrophile that was stable and one with whose chemistry we were familiar. Also, we reasoned that the product might be interesting because a part of the chemistry of dicyanocyclopentadiene relates to its incorporation into mixed fulvalene structures. For example, the hydrocarbon sesquifulvalene (II),



II

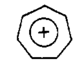
which may be described by the resonance forms IIa and IIb, appears to be quite unstable.[29] A variety of heterosesquifulvalenes[30] have been prepared that exhibit enhanced stability. The coupling of DCCP into mixed fulvalene systems, because of the strong effect of the electron-deficient cyano groups, should act to enhance the stability of such compounds. This worked well, in one case, in the formation of 10,11-dicyanopentaphenafulvalene (III).[31]



III

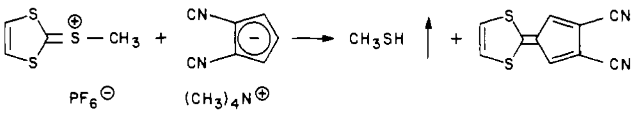
The replacement of a –CH=CH– group of a carbocycle by a chalcogenide heteroatom, such as sulfur, results in a species isoelectronic with the original ring (referred to in this paper as a heterosesquifulvalene). Therefore, the 1,3-dithiolium cation (IV) becomes a heteroanalogue of tropylium (V).

IV

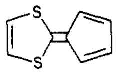


V

When (TMA)(DCCP) and 2-(methylthio)-1,3-dithiolium cation[10] solutions are mixed, orange needles form and methyl mercaptan is evolved.



The elemental analysis of the solid and its NMR spectrum (Me_2SO-d_6) are entirely consistent with the heterosesquifulvalene 2-(3,4-dicyanocyclopentadienylidene)-1,3-dithiole (VI). The parent heterosesquifulvalene 2-(cyclopentadienylidene)-1,3-dithiole (VII) has previously been reported.[32] The NMR spectrum reported for VII consisted of



VII

two singlets at δ 6.32 and 6.60 in the ratio of 4 H to 2 H, respectively. The authors assigned the low-field line to the dithiole ring protons and the high-field line to the carbon ring protons. It seems amazingly coincidental that the protons of the cyclopentadiene moiety do not appear as a multiplet.[33] The chemical shift of the dithiole ring in TTF is δ 6.25, at slightly higher field than in VII. This implies a small contribution, in VII, of the dipolar form.

For VI, the situation is different. The NMR spectrum appears as two singlets, with both lines coming at quite low fields, in the aromatic region, e.g. δ 7.17 and 8.05. These data imply a large contribution from the dipolar structure. Comparison of the chemical shift of the DCCP anion resonances, δ 6.27 (d, 2 H) and 5.55 (t, 1 H), with the DCCP portion of III,[31] δ 7.06, provides evidence for analogously large dipolar-form contributions.

Registry No. VI, 87829-78-5; Co(DCCP)$_4$(TMA)$_2$, 87841-53-0; Ag^{I}DCCP, 87829-77-4; (TMA)(DCCP), 42491-32-7; DCCP, 45662-26-8; 2-(methylthio)-1,3-dithiolium hexafluorophosphate, 87829-79-6; 2-(methylthio)-1,3-dithiolium iodide, 53059-74-8.

Supplementary Material Available: Listings of observed and calculated structure factors, hydrogen positional parameters, and thermal parameters and their errors, Table III (10 pages). Ordering information is given on any current masthead page.

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