Fig. 2. A perspective view of the anionic chain in $BaCoO_3$.

The structure was found to be isostructural with $BaNiO_3$, and the positional parameters are almost the same as those of $BaNiO_3$. Within the BaO_3 layers, the O—O distance is 2·511 Å, while the O—O distance between the layers is 2·783 Å. The Ba—O distance within the layer is 2·828 Å. Although these lengths must be equal for ideal hexagonal close packing of Ba and O, the O—O distance within the layer is much shorter than that between layers. These three oxygens forming short O—O distances make a triangular plane sharing the faces of the CoO_6 octahedra columns. The Co^{4+} ions in the columns face each other at a very short distance of 2·38 Å (2·41 Å in $BaNiO_3$); this will produce a large electrostatic repulsion between the metal ions. As the O atoms of face-sharing triangles mutually approach, as mentioned above, the O ions are considered to screen the Coulomb interaction between Co^{4+} ions and weaken the repulsion. The Ba^{2+} ions play a role in adjusting the spacing between these chains.

However, $BaNiO_3$ does not have an ideal hexagonally close-packed arrangement of Ba and O ions, but all the O ions are remarkably close to Ni ions and form a trigonally distorted octahedron; the Ni^{4+}—O distance is much shorter than that expected from the ideal ionic model (Takeda, Kanamaru, Shimada & Koizumi, 1976).

Figs. 1 and 2 show the Co environment and the hexagonal close packing of the Ba and O ions in $BaCoO_3$.

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Bis(3,5-dimethyl-1,2-dithiolium) Tetrachlorocobaltate(II)

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Abstract. $C_{10}H_{14}Cl_4CoS_4$, $M_r = 463\cdot2$, monoclinic, $C2/c, a = 17\cdot67\,(2), b = 7\cdot70\,(1), c = 15\cdot78\,(2)$ Å, $\beta = 122\cdot22\,(1)°$ from diffractometer measurements (Mo $K\bar{\alpha}$ radiation); $V = 1817\cdot9$ Å³, $Z = 4$, $F(000) = 924$, $\mu = 17\cdot70$ cm⁻¹. The compound is isostructural with the corresponding tetrachloroferrate(II) [Freeman, Milburn, Nockolds, Mason, Robertson & Rusholme, *Acta Cryst.* (1974), B30, 886–910].

Introduction. Blue-green crystals of the title compound (Heath, Martin & Stewart, 1969a,b)* suitable for X-ray examination were obtained from ethanolic HCl. Systematic absences (from Weissenberg and precession photographs) hkl, $h + k$ odd and $h0l$, l odd indicated space groups Cc or $C2/c$. The latter was assumed since

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* Hereafter HMS.

$(C_5H_7S_2)_2CoCl_4$ appeared isostructural with the $(FeCl_4)^{2-}$ complex (Hoskins, 1969) which was refined in $C2/c$. Data were collected for $h0-8l$ with $\theta_{max} = 27.5°$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\bar{\alpha}$ radiation). This gave 1939 unique reflexions of which 1520 with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The initial atomic coordinates were taken from Freeman et al. (1974).* The SHELX-76 system of crystallographic programs (Sheldrick, 1976) was used for all calculations. Complex neutral atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). Weighted full-matrix least-squares refinement converged at R $(= \Sigma ||F_o| - |F_c||/\Sigma |F_o|) = 0.033$ for the 1520 observed reflexions, and R_w $[= \Sigma w^{1/2}(||F_o| - |F_c||)/\Sigma w^{1/2}|F_o|] = 0.046$, where $w = [\sigma^2(F) + 0.076F^2]^{-1}$. In the final cycle all shifts in parameters were less than their standard deviations. Positional parameters are given in Table 1,† and bond lengths and angles in Table 2 (the atomic numbering corresponds to that in FMNMRR).

Discussion. $(C_5H_7S_2)_2CoCl_4$ is isostructural with the purple $(FeCl_4)^{2-}$ salt which provides a notable example of interionic charge transfer associated with well defined molecular interactions and absorption in the visible spectrum (HMS, FMNMRR). The two structures have almost identical cell and atomic parameters and are characterized by weak S···Cl bonding between

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* Hereafter FMNMRR.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32399 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses (all ×10⁴)*

	x	y	z
Co	0	10984 (1)	7500
Cl(1)	779 (1)	12664 (1)	7047 (1)
Cl(2)	997 (1)	9358 (1)	8878 (1)
S(1)	916 (1)	7431 (1)	6918 (1)
S(2)	476 (1)	7327 (1)	5447 (1)
C(1)	1910 (2)	6457 (4)	7329 (2)
C(2)	2063 (2)	5989 (4)	6594 (3)
C(3)	1401 (2)	6314 (4)	5611 (3)
C(4)	2528 (3)	6151 (6)	8422 (3)
C(5)	1459 (4)	5834 (7)	4730 (3)
H(1)	2503 (46)	4818 (104)	8636 (56)
H(2)	3210 (37)	6510 (66)	8667 (38)
H(3)	2390 (26)	6510 (50)	8773 (31)
H(4)	2586 (32)	5471 (54)	6758 (33)
H(5)	1121 (59)	5455 (104)	4329 (63)
H(6)	1503 (46)	6886 (92)	4493 (57)
H(7)	2019 (36)	5282 (61)	5008 (36)

the dithiolium cations and $(MCl_4)^{2-}$ anions. The anion lies on a twofold axis and is distorted from tetrahedral symmetry. The Co—Cl bonds are slightly shorter than Fe—Cl, but in both compounds M—Cl(1) is 0.04 Å less than M—Cl(2), and the slight flattening observed in the $(FeCl_4)^{2-}$ tetrahedron is also present in $(CoCl_4)^{2-}$, to about half the extent. The geometries of the dithiolium cations are identical within the experimental estimated standard deviations.

In the lattice the cations alternate with pairs of Cl ligands in an infinite sequence along **c** (Fig. 1). In the dithiolium halides (Hordvik, 1966) the disulphide group is similarly involved in linear S—S···X and triangular S_2X interactions (Fig. 2). The structures of the $(MCl_4)^{2-}$ complexes reflect the reorganization of the lattice which occurs when the halide ions are brought close together by coordination to the metal. The close

Table 2. *Bond distances (Å) and angles (°), with e.s.d.'s in parentheses*

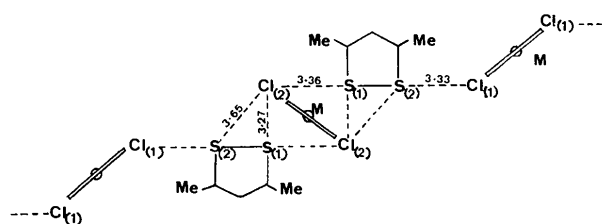|			
Co—Cl(1)	2.266 (1)	S(1)—C(1)	1.690 (4)
Co—Cl(2)	2.306 (1)	S(2)—C(3)	1.701 (4)
S(1)—S(2)	2.020 (2)	C(1)—C(2)	1.373 (5)
		C(1)—C(4)	1.489 (7)
Mean C—H	0.92 (1)	C(3)—C(2)	1.379 (5)
		C(3)—C(5)	1.493 (7)
Cl(1)—Co—Cl(1')	110.3 (1)	S(1)—C(1)—C(4)	119.0 (3)
Cl(1)—Co—Cl(2)	108.7 (1)	C(2)—C(1)—C(4)	125.8 (4)
Cl(1)—Co—Cl(2')	107.5 (1)	C(1)—C(2)—C(3)	118.3 (3)
Cl(2)—Co—Cl(2')	114.2 (2)	S(2)—C(3)—C(2)	115.1 (3)
S(2)—S(1)—C(1)	96.2 (2)	S(2)—C(3)—C(5)	120.5 (3)
S(1)—S(2)—C(3)	95.4 (2)	C(2)—C(3)—C(5)	124.4 (4)
S(1)—C(1)—C(2)	115.2 (3)		
		Mean	
Mean H—C(Me)—C	111.8	H—C(Me)—H	106.7

Fig. 1. Intermolecular interactions in dithiolium tetrachlorocobaltate, with distances in Å.
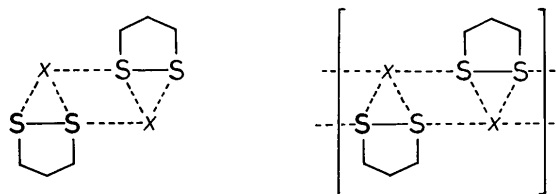

Fig. 2. Two generalized schemes of anion–cation interactions in dithiolium halides (adapted from Hordvik, 1966).

similarity of the interionic relationships in the two $(MCl_4)^{2-}$ complexes suggests that there is little dependence of ground-state partial bonding on the metal d^n population. The shift of the optical charge-transfer transition to lower energy in the Fe compound parallels the greater ease of reduction of Fe^{II}.

We have also prepared the hitherto unknown $(CuCl_4)^{2-}$ analogue. Remarkably, it is not isostructural with the $(CoCl_4)^{2-}$ and $(FeCl_4)^{2-}$ complexes, although its triclinic cell parameters are very closely related to those of the monoclinic cells of the Co^{II} and Fe^{II} complexes. Preliminary X-ray and infrared data suggest two different environments for the dithiolium cations. It appears, therefore, that the known tendency of $(CuCl_4)^{2-}$ to occur as a considerably flattened tetrahedron is associated with further reorganization of the lattice. We hope to report the structure of the Cu^{II} complex in due course.

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Terephthalonitrile

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Abstract. Eastman-Kodak $C_6H_4(CN)_2$ was recrystallized from glacial acetic acid; triclinic, $P\bar{1}$ (No. 2), $Z = 1$, $a = 7\cdot318$ (3), $b = 7\cdot544$ (3), $c = 3\cdot841$ (2) Å, $\alpha = 80\cdot45$ (3), $\beta = 93\cdot57$ (3), $\gamma = 127\cdot44$ (1)°, $V = 165\cdot8$ Å^3, $D_c = 1\cdot283$ g cm^{-3}. (The standard setting has $a = 6\cdot583$, $b = 7\cdot318$, $c = 3\cdot841$ Å, $\alpha = 93\cdot57$. $\beta = 96\cdot94$, $\gamma = 114\cdot52$°. It can be obtained from the setting used in the main body of the paper by the transformation $\bar{1}10/100/001$.) The molecular dimensions are normal except that the nitrile groups are bent $0\cdot5$° out of the plane of the ring. The molecules are packed parallel to one another with antiparallel nitrile groups in contact.

Introduction. 526 independent reflections were collected for $0 < \theta \leq 24°$ on a Hilger & Watts four-circle automated diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). The 11 most intense reflections appeared to suffer from extinction and were given zero weight in the least-squares calculations; for the 47 reflections for which I_0 was < 0, $I = 0$ was used. The crystal used was $0\cdot11 \times 0\cdot32 \times 0\cdot20$ mm; no absorption corrections were made ($\mu = 0\cdot86$ cm^{-1}). The

intensities of two check reflections decreased by 20% during the course of the data collection; corrections were made for this slow sublimation or decomposition. The space group was assumed to be $P\bar{1}$ since the molecule should have a center of symmetry. A trial structure was found from Patterson and Fourier maps and refined by full-matrix least squares, with anisotropic thermal parameters for the C and N atoms and isotropic thermal parameters fixed at $5\cdot0$ Å^2 for the H atoms. For details of the experimental arrangements and for the weights, calculations and programs used, see Chow & Britton (1974). The refinement converged with $R = 0\cdot111$; if the 11 intense reflections are omitted, $R = 0\cdot096$; if the 116 weakest reflections are omitted, which corresponds roughly to omitting those reflections with $I < 2\sigma(I)$, $R = 0\cdot069$. The final positional parameters are given in Table 1.*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32398 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.