

chloro and bromo analogs, we regarded the linear chain as consisting of alternately arranged tetragonal-bipyramidal [Pt(en)₂I₂]²⁺ and square-planar [Pt(en)₂]²⁺ units, where 2.704 (11), 2.726 (9) Å and 3.115 (11), 3.039 (9) Å are assigned as the Pt^{IV}–I and Pt^{II}–I distances respectively. The thermal parameters of N(1), N(2), C(1) and C(2) are normal. Therefore, the dimensions and conformation of the Pt^{II} and Pt^{IV} species should be the same except for the Pt–I bond; this is because such differences between the Pt^{II} and Pt^{IV} species would result in high thermal parameters in the average subcell structure.

The distances N(1)–O(1), N(1)–O(2), N(2)–O(1), and N(2)–O(2) indicate that there are hydrogen bonds between these atoms. These hydrogen bonds should contribute to the formation of the infinite chain, as was observed for the chloro and bromo analogs.

The ratio of the Pt^{IV}–I and Pt^{II}–I distances is 0.93, which is much higher than the ratios of the Pt^{IV}–halogen and Pt^{II}–halogen distances reported for the bromo (0.86, 0.87) and chloro (0.76) analogs (Ma-

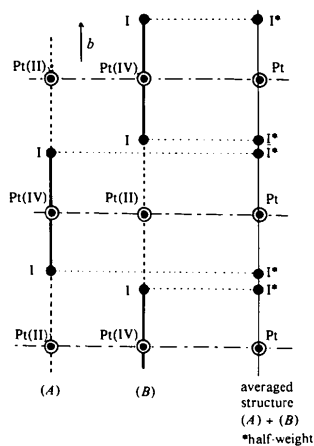


Fig. 2. An illustration of the disorder along *b*.

tsumoto, Yamashita & Kida, 1978*b*). The above results imply that the difference in the oxidation states between Pt^{IV} and Pt^{II} atoms is reduced in the order: chloro, bromo and iodo analogs.

Recently, we evaluated the quantitative values of the oxidation states of these complexes from the X-ray photoelectron spectra (ESCA), and confirmed that the ESCA results were consistent with the above structural results (Yamashita, Matsumoto & Kida, 1978).

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Tetrakis(*N,N'*-diethylthiourea)cobalt(II) Diperchlorate

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Abstract. [Co(C₅H₁₂N₂S)₄](ClO₄)₂, C₂₀H₄₈Cl₂CoN₈O₈S₄, orthorhombic, *Pbcn*, *a* = 19.447 (4), *b* = 13.939 (4), *c* = 14.360 (5) Å, *Z* = 4, *D*_o = 1.36 (1), *D*_c

= 1.342 Mg m⁻³. The structure contains discrete Co[S=C(NHCH₂CH₃)₂]₄²⁺ ions with point symmetry 2. Each Co atom is ligated by four S atoms having a

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flattened-tetrahedral arrangement; dihedral angles involving the S—Co—S planes are 78.2 (2), 78.7 (2) and 90.5 (3)°. The S—Co—S angles within the coordination polyhedron range from 98.3 (2) to 115.7 (2)°. Both crystallographically unique Co—S distances [2.295 (6), 2.293 (5) Å] are equivalent. The perchlorate group and one ethylamino group are disordered.

Introduction. We have been interested in characterizing model M^{II} mercaptide ($M = \text{Cu, Co, Zn}$) complexes to understand better the spectral and structural features of analogous chromophores present in various proteins. Because mercaptide complexes of Co^{II} tend to be oxidatively and photolytically unstable, it is difficult to obtain resonance Raman spectra of the Co^{II} —sulfur modes. Resonance-enhanced modes of this type are potentially useful structural probes for Co^{II} -substituted protein sites. Co^{II} complexes of thioureas are much more stable, and we have been able to investigate them thoroughly (Salama, Schugar & Spiro, 1979). While thioureas and mercaptides differ chemically, they do have similar optical electro-negativities. Approximately tetrahedral Co^{II} complexes of thioureas exhibit ligand-field and charge-transfer spectra (Piovesana & Furlani, 1968) similar to those observed for structurally analogous Co^{II} mercaptide complexes (Mastropaolo, Tich, Potenza & Schugar, 1977). To facilitate our spectroscopic studies, we chose to synthesize and characterize structurally a tetrakis Co^{II} thiourea complex whose gegenion (ClO_4^-) spectrally is transparent over the visible and near ultra-violet region.

Blue prisms of the title complex crystallized from cooled isopropyl alcohol solutions which contained a 1:4 molar ratio of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the ligand. A single crystal of dimensions $0.25 \times 0.23 \times 0.21$ mm, mounted on a glass fiber, was used. Weissenberg photographs showed systematic absences for $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h + k = 2n + 1$, along with mmm reciprocal-lattice symmetry, indicating space group $Pbcn$. Assuming four molecules per cell, the observed (gradient) and calculated densities agreed well. Data were collected at 296 ± 1 K with a Syntex $P2_1$ automated diffractometer (θ - 2θ scan) using graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.71069$ Å). A total of 810 reflections ($4 < 2\theta < 42^\circ$) having $F^2 > 3\sigma(F^2)$ were considered observed, corrected for Lp and absorption effects ($\mu = 0.847 \text{ mm}^{-1}$ for $\text{Mo } K\alpha$ radiation), and used in the refinement. The relatively small number of 3σ data points is attributable in part to thermal motion in the crystal; the Wilson plot temperature factor was $B = 4.8 \text{ \AA}^2$. Three standard reflections, measured at 47 reflection intervals, remained constant to $\pm 2\%$ throughout the data-collection period.

The structure was solved by direct methods and refined by full-matrix least-squares techniques using

programs described previously (Fawcett, Ushay, Rose, Lalancette, Potenza & Schugar, 1979). Neutral-atom scattering factors and anomalous-dispersion corrections for Co, S, and Cl were obtained from *International Tables for X-ray Crystallography* (1974). An E map calculated using 300 phases from the starting set having the highest combined figure of merit revealed all non-hydrogen atoms except the perchlorate O atoms and three atoms from an ethylamino group [N(1), C(2) and C(3)].

A difference Fourier map revealed a large number of small peaks surrounding the Cl atom as well as several broad, overlapping peaks in the vicinity of N(1), suggesting disorder at these sites. From electron densities in the difference map, 12 peaks in the vicinity of the Cl atom were located. These peaks were consistent with three sets of perchlorate O atoms with approximate occupancies of 45, 30 and 25%.* Several methods for refining the perchlorate disorder were attempted. With the Cl atom at one site and fixed O occupancies, refinement yielded $R_F = \sum |F_o| - |F_c| / \sum |F_o| = 0.076$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.089$; however, convergence was difficult to obtain and several O temperature factors were as large as 40 \AA^2 . Bond distances and angles within the perchlorate group also showed an unusually large span. Rigid-body refinement using fixed Cl—O distances (1.41 Å) and tetrahedral O—Cl—O angles gave values of $R_F = 0.109$ and $R_{wF} = 0.114$ at convergence; for this refinement, the Cl atom was allowed to occupy three sites, and both Cl and O occupancies were refined. Finally, a model in which the Cl atom was allowed to occupy three sites gave $R_F = 0.073$ and $R_{wF} = 0.086$ when all coordinate and temperature factors as well as Cl and O occupancies were allowed to vary. Using Hamilton's (1965) R -factor test, the decrease in R_{wF} for the third model is significant. For this model, which we report, Cl—O distances ranged from 1.25 (6) to 1.67 (9) Å with an average of 1.42 Å while the O—Cl—O angles ranged from 90 (3) to 127 (4)° with an average of 109° . These averages agree well with values reported for perchlorate groups where disorder was not a problem (Ou, Miskowski, Lalancette, Potenza & Schugar, 1976) while the ranges are approximately the same as those found for other structures with disordered perchlorate groups (Jungst & Stucky, 1974; Curtis, McCormick & Waters, 1973).

Several attempts to model the disordered ethylamino group, by allowing it to occupy either two or three sites, proved unrewarding. The best model appeared to be one with occupancy of one site. This gave relatively large temperature factors and unusual bond distances about C(2). Similar difficulties with

* At an equivalent point of refinement, isotropic convergence, models with zero, 4, 8, and 12 O atoms with appropriate atom multipliers gave R_F values of 0.219, 0.189, 0.196 and 0.163, respectively.

alkyl groups have been encountered previously (Potenza, Johnson & San Filippo, 1976).

H atom positions were calculated by methods described previously (Fawcett, Ou, Potenza & Schugar, 1978). Before anisotropic refinement, they were assigned fixed isotropic temperature factors equal to $B_N + 1$, where B_N is the temperature factor of the atom bonded to H. Refinement of all non-hydrogen coordinates, using anisotropic thermal parameters for Co, Cl, S and N atoms, gave final values of $R_F = 0.073$ and $R_{wF} = 0.086$. For the final cycle, all parameter changes for the ordered atoms were less than 0.1σ , where σ is the e.s.d. obtained from the inverse matrix. A final difference map showed a general background of $\pm 0.5 \text{ e } \text{Å}^{-3}$ and revealed no significant features; the largest positive peak was smaller than the largest negative peak, indicating that the model chosen gives a good account of the electron density in the cell. Atom

Table 1. Final atomic coordinates

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses.

	x	y	z
Co	$\frac{1}{2}$	0.3572 (2)	$\frac{1}{2}$
S(1)	0.4255 (4)	0.2691 (4)	0.1603 (3)
S(2)	0.4507 (3)	0.4459 (3)	0.3666 (3)
Cl(47)*	0.1940 (8)	0.3631 (7)	0.306 (1)
Cl(30)	0.195 (1)	0.357 (2)	0.295 (1)
Cl(23)	0.202 (2)	0.362 (2)	0.300 (2)
N(1)	0.380 (1)	0.097 (1)	0.210 (1)
N(2)	0.3688 (9)	0.212 (1)	0.319 (1)
N(3)	0.3686 (7)	0.508 (1)	0.230 (1)
N(4)	0.3965 (8)	0.619 (1)	0.341 (1)
C(1)	0.393 (1)	0.186 (1)	0.236 (1)
C(2)	0.393 (2)	0.060 (2)	0.098 (2)
C(3)	0.452 (2)	0.021 (3)	0.118 (3)
C(4)	0.340 (1)	0.150 (1)	0.390 (1)
C(5)	0.330 (1)	0.200 (1)	0.480 (1)
C(6)	0.4026 (9)	0.529 (1)	0.308 (1)
C(7)	0.329 (1)	0.573 (1)	0.172 (1)
C(8)	0.316 (1)	0.525 (1)	0.079 (1)
C(9)	0.430 (1)	0.653 (1)	0.424 (1)
C(10)	0.487 (1)	0.716 (2)	0.405 (2)
O(1)†	0.201 (1)	0.272 (2)	0.318 (2)
O(2)	0.198 (4)	0.411 (6)	0.224 (5)
O(3)	0.132 (2)	0.411 (2)	0.326 (2)
O(4)	0.255 (2)	0.399 (3)	0.349 (2)
O(5)	0.274 (9)	0.374 (12)	0.346 (12)
O(6)	0.156 (4)	0.386 (6)	0.395 (6)
O(7)	0.185 (3)	0.280 (4)	0.249 (4)
O(8)	0.199 (3)	0.433 (4)	0.246 (4)
O(9)	0.205 (3)	0.447 (8)	0.312 (5)
O(10)	0.197 (2)	0.307 (4)	0.387 (6)
O(11)	0.252 (4)	0.330 (4)	0.232 (4)
O(12)	0.138 (3)	0.331 (3)	0.236 (3)

* Atom numbers for the Cl atoms correspond to per cent occupancy at that site.

† Occupancy factors for the O atoms are as follows: O(1)–O(4), 0.47; O(5)–O(8), 0.23; O(9)–O(12), 0.30. Thus, atoms O(1)–O(4) are bound to Cl(47), etc.

parameters* are given in Table 1. A view of the structure is given in Fig. 1.

Discussion. The structure contains discrete $\text{Co}[\text{SC}(\text{NHCH}_2\text{CH}_3)_2]_2^{2+}$ ions with point symmetry 2. The S_4 ligand donor set has a flattened-tetrahedral arrangement as evidenced by the $\text{S}(1)\text{--Co--S}(1')/\text{S}(2)\text{--Co--S}(2')$, $\text{S}(1)\text{--Co--S}(2)/\text{S}(1')\text{--Co--S}(2')$ and $\text{S}(1)\text{--Co--S}(2')/\text{S}(1')\text{--Co--S}(2)$ dihedral angles of $78.2(2)$, $78.7(2)$, and $90.5(3)^\circ$, respectively. Bond angles within the CoS_4 unit span the range $98.3(2)$ to $115.7(2)^\circ$. Both Co--S distances [$2.295(6)$, $2.293(5)$ Å] are equivalent. Observed bond angles as well as metal–ligand and ligand bond distances of the title complex closely correspond to those reported for $\text{Co}[\text{SC}(\text{NHCH}_2\text{CH}_3)_2]\text{Cl}_2$ (Bonamico, Dessy, Fares & Scaramuzza, 1973) in which Co is ligated by two S and two Cl atoms. Moreover, the observed Co--S bond distances correspond closely to the Co--S (mercaptide) bond distance of $2.272(2)$ Å reported for $\text{Co}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2$ (Mastropaolo *et al.*, 1977). This result is in harmony with the electronic-structural similarity between Co^{II} –mercaptide and Co^{II} –thiourea chromophores noted above.

* Lists of structure factors, thermal parameters, and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34275 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

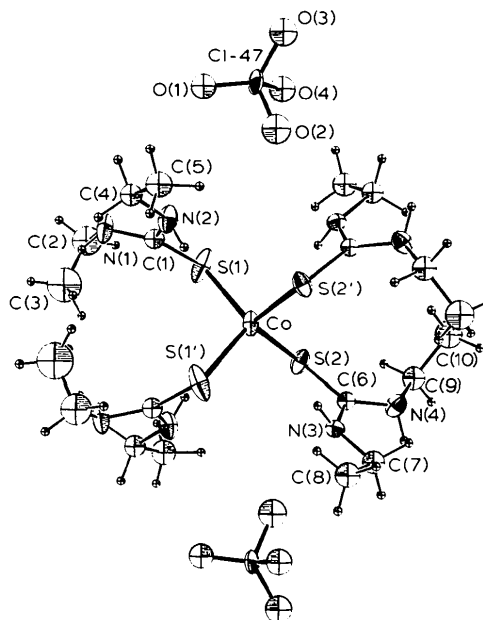


Fig. 1. View of the title complex showing the atom-numbering scheme. The ClO_4^- group shown is that having the highest (47%) occupancy.

Of particular interest to our resonance Raman studies is the nature of the $\text{Co}^{\text{II}}-\text{S}$ bonding in the title complex. Within experimental error, one thiourea group is planar while the second deviates from planarity. Atom displacements (in Å) from the least-squares planes are -0.017 (6), -0.02 (2), -0.02 (2) and 0.06 (2), respectively, for the S(1), N(1), N(2), C(1) unit and 0.002 (5), 0.00 (2), 0.00 (2) and -0.01 (2), respectively, for the S(2), N(3), N(4), C(6) unit. Bonding of Co^{II} to a thiourea can involve an sp^2 orbital localized on the S atom as well as a delocalized π -symmetry molecular orbital. Bonding of the former type is characterized by a $\text{Co}-\text{S}-\text{C}/\text{S}-\text{C}-\text{N}$ dihedral angle in the range 17 to 34° ; bonding of the latter type was indicated by a considerably larger dihedral angle (75.8°) reported for $\text{Co}[\text{SC}(\text{NH}_2)_2]_4(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Spofford, Boldrini, Amma, Carfagno & Gentile, 1970). While sp^2 -type bond angles for thiourea complexes normally span the range 108 – 116° , the $\text{Co}-\text{S}-\text{C}$ angle associated with the large dihedral angle above was 103.0° . The four $\text{Co}-\text{S}-\text{C}/\text{S}-\text{C}-\text{N}$ angles in the title complex range from 36 to 48° while the two unique $\text{Co}-\text{S}-\text{C}$ angles are 104.1 (7) and 103.5 (6) $^\circ$. Thus, $\text{Co}-\text{S}$ bonding in the title complex appears to lie at the boundary where 'pure' sp^2 bonding becomes mixed with π -symmetry Co -thiourea interactions.

The ClO_4^- ions appear to be loosely held in lattice holes by Coulombic forces and weak hydrogen bonds to neighboring amine groups. All O atoms involved in hydrogen bonding have relatively small temperature factors. Conversely, those O atoms far removed from the N atoms or which make poor hydrogen-bonding angles have large temperature factors.

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Structure of *cis*-Di- μ -methoxy-bis(η^5 -cyclopentadienyl)nitrosylchromium

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Abstract. $[\text{Cr}_2(\text{CH}_3\text{O})_2(\text{C}_5\text{H}_5)_2(\text{NO})_2]$, $\text{C}_{12}\text{H}_{16}\text{Cr}_2\text{N}_2\text{O}_4$, orthorhombic, *Pnma*, $a = 12.810$ (7), $b = 17.575$ (6), $c = 6.431$ (3) Å, $Z = 4$, $V = 1447.8$ Å³, $M_r = 356.2$, $D_c = 1.63$ Mg m⁻³, $F(000) = 728$, $\mu(\text{Mo } K\alpha) = 1.58$ mm⁻¹, $R = 0.068$ for 718 reflections. The molecule has a plane of symmetry passing through the O and C atoms of the bridging methoxy groups. The Cr_2O_2 ring is buckled, with the two Cr_2O planes inclined at 156° . The Cr–O lengths are 1.955, 1.960 (6) Å and the Cr–Cr distance is 2.882 (2) Å.

The O–Cr–O angle is 83.0 (3) $^\circ$ and the Cr–O–Cr angles are 94.6 (4), 95.0 (3) $^\circ$.

Introduction. The four-membered ring M_2X_2 is a common feature of binuclear metal complexes. The preparation of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})X]_2$, where $X = \text{SPh}$, NMe_2 , etc. (Ahmad, Bruce & Knox, 1966) made available an opportunity to examine the effect on the ring geometry of changes in the bridging ligand X , and the molecular structures of *trans*- $[(\eta^5-$