

Crystal Structures and Interrelationships of the Blue and Green Conformational Isomers of Tetrakis(trimethylarsine sulphide)cobalt(II) Perchlorate†

Patricia C. Tellinghuisen, Ward T. Robinson,* and Cuthbert J. Wilkins*
Chemistry Department, University of Canterbury, Christchurch, New Zealand

Blue and green compounds, $[\text{Co}(\text{Me}_3\text{AsS})_4][\text{ClO}_4]_2$, which are conformationally isomeric, crystallise when cobalt(II) perchlorate reacts with trimethylarsine sulphide in ethanol and acetone respectively. Their crystal structures show that the cation field spreading from the AsMe_3 groups permits side-by-side packing of the cations into columns with the methyl groups pointing outwards. The column packing, together with S–Co–S valence angles and S–Co–S–As torsion angles, differs in the two isomers. For the blue isomer the S–Co–S angles fall in pairs: 120.4, 117.0; 108.6, 107.1; 102.5, 102.0°. For the green isomer two angles are 90° and four are close to 120°, with the sulphur atoms forming a tetragonal sphenoid. The green isomer and the nickel compounds $[\text{Ni}(\text{Me}_3\text{AsS})_4][\text{ClO}_4]_2$ and $[\text{Ni}(\text{Me}_3\text{AsS})_4][\text{BF}_4]_2$ are isomorphous. For these nickel compounds the sphenoidal configuration is associated with ligand-field stabilisation. It is suggested that the ligand-field effect, though smaller for cobalt, helps stabilise the green isomer.

The co-ordination behaviour of first-row transition elements towards trimethylarsine sulphide and related ligands has been investigated in this laboratory.^{1,2} The electronic spectrum and magnetic moment of the blue compound $[\text{Co}(\text{Me}_3\text{AsS})_4][\text{ClO}_4]_2$ were taken as evidence for 'tetrahedral' co-ordination.³ Subsequent structural studies on cobalt–thiourea complexes of the same generic type $[\text{CoL}_4]^{2+}$ have all shown some deviation from the regular tetrahedral configuration.^{4–7} Our interest in cobalt complexing by trimethylarsine sulphide was renewed by the observation that, whereas the blue compound separated from ethanol, a green isomer crystallised from acetone. The two isomers give identical solution spectra in both nitromethane and acetone, corresponding to the reflectance spectrum of the blue form (Table 1). The ν_3 bands of the two forms are quite similar, with the colour difference due mainly to the stronger absorption of blue wavelengths by the charge-transfer band of the green form. The ν_2 band of the green isomer is more highly structured than that of the blue.⁸ The i.r. spectrum of the green compound shows a more complex $\nu(\text{Co–S})$ band than does the blue, and the magnetic moment of the green (4.75 ± 0.10 B.M. at 20 °C) is higher than that of the blue (4.40 ± 0.10 B.M.), indicating greater spin–orbit coupling. These properties suggest that the co-ordination pattern for the green form deviates further from regular tetrahedral. We now report crystal-structure determinations which establish the differences in the co-ordination environments.

Results and Discussion

Cobalt Co-ordination.—Since the spectrum of the crystalline blue compound matches that of the solution it is inferred that this isomer has the more stable co-ordination configuration characteristic of the 'free' cation. The configuration of the green isomer enables a slightly smaller unit-cell volume and is only stabilised within the crystal. The two forms of the cation have the same connectivity and the compounds are therefore conformational isomers.

† Supplementary data available (No. SUP 56208, 9 pp.): thermal parameters, approach distances, angles in thiourea complexes, stereodiagrams. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. $\approx 9.27 \times 10^{-24}$ A m².

Table 1. Electronic spectral bands (10^3 cm^{-1})

	$\tilde{\nu}_3^a$	$\tilde{\nu}_2^b$
Solution in nitromethane ^c	15.29(530), 14.41(780), 13.40(720)	7.67(163), 6.23(161)
Blue isomer ^d	15.43, 14.41, 13.57	7.70, 6.63
Green isomer ^d	15.58, 15.11, 14.41, 13.87	8.33, 7.52, 6.99, 6.45, 5.71, 5.00

^a $^4A_2 \rightarrow ^4T_2$ (without spin–orbit coupling). ^b $^4A_2 \rightarrow ^4T_1$ (without spin–orbit coupling). ^c $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in parentheses. ^d Solid state.

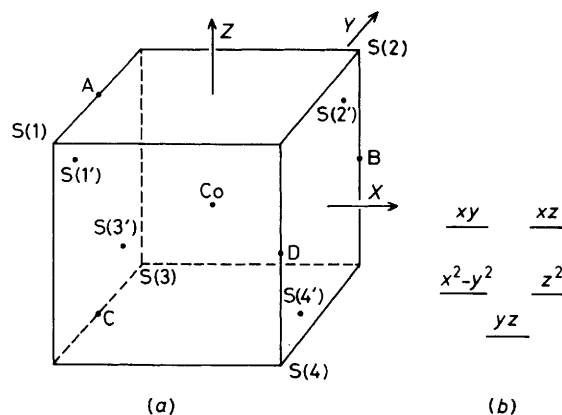


Figure 1. (a) Bond directions in relation to a regular tetrahedral configuration. (b) Schematic *d*-orbital energy-level diagram for sphenoidal configuration, with bond directions through A, B, C, and D

The structure determination confirms that the cobalt co-ordination deviates further from T_d in the green isomer than in the blue, but in both cases there is retention of near equivalence of opposite pairs of S–Co–S bond angles (Table 2). A similar correlation of bond-angle pairs in thiourea complexes has been described in terms of a flattening of an idealised regular co-ordination tetrahedron along with a counter rotation of planes.^{4,6} Thus in Figure 1 the angles S(1)–Co–S(2) and S(3)–Co–S(4) would be spread and the planes S(1)CoS(2) and

Table 2. Valence, dihedral, and torsion angles (°)

Valence angles	Blue isomer	Green isomer
S(1)-Co-S(2) ^a , S(3)-Co-S(4) ^a	117.0(4), 120.4(4)	119.6(3), 121.0(3)
S(1)-Co-S(4), S(2)-Co-S(3)	108.6(4), 107.1(4)	120.4(3), 119.7(3)
S(1)-Co-S(3), S(2)-Co-S(4)	102.0(4), 102.5(4)	89.8(3), 89.7(3)
Co-S(1)-As(1)	106.5(4)	111.2(3)
Co-S(2)-As(2)	106.6(4)	109.2(4)
Co-S(3)-As(3)	109.0(4)	112.0(4)
Co-S(4)-As(4)	108.9(4)	110.2(3)
Dihedral angles		
S(1)-Co-S(2)/S(3)-Co-S(4)	86.4(4) ^b	70.4(4) ^c
Torsion angles^d		
As(1)-S(1)-Co-S(2)	+60.6(4)	+61.1(4)
As(2)-S(2)-Co-S(1)	+65.9(4)	+48.7(4)
As(3)-S(3)-Co-S(4)	-83.2(4)	+57.6(4)
As(4)-S(4)-Co-S(3)	-50.1(4)	+47.4(4)

^a Paired. ^b Signifying counter rotation, 3.6°. ^c Would signify counter rotation, 19.6°. ^d For the green isomer the angles As(1)-S(1)-Co-S(3), As(2)-S(2)-Co-S(4), As(3)-S(3)-Co-S(1), and As(4)-S(4)-Co-S(2) are respectively -174.3(4), +174.0(4), -176.4(4), and +172.4(4)°. Clockwise rotations (+), anticlockwise (-).

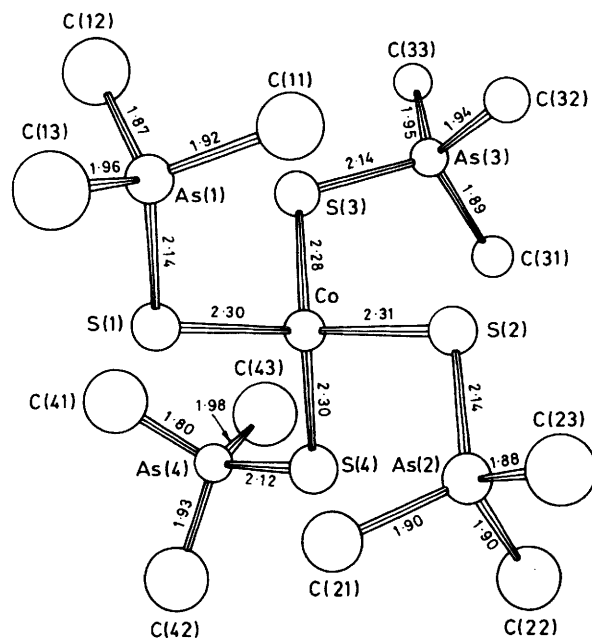


Figure 2. The cation of the blue isomer viewed down the Z axis of the cube in Figure 1(a). E.s.d.s for bond lengths: Co-S, 0.01; As-S, 0.01; As-C, 0.04 Å

S(3)CoS(4) counter-rotated. The bond directions would then be defined by the pairs of points S(1'), S(3') and S(2'), S(4') on opposite faces of the circumscribing cube, and in general this would lead to three non-equivalent pairs of bond angles. In terms of this description the plane twist for the blue isomer is 3.6° and for the green isomer is 19.6°. However, in the latter structure new symmetry elements appear because two pairs of bond angles are equivalent at values close to 120°, with the third pair at 90°.

As regards the structures of the complete cations, that of the blue isomer shows the AsC₃ groups forming a buckled swastika pattern (Figure 2, a view down the Z axis of the cubic frame of

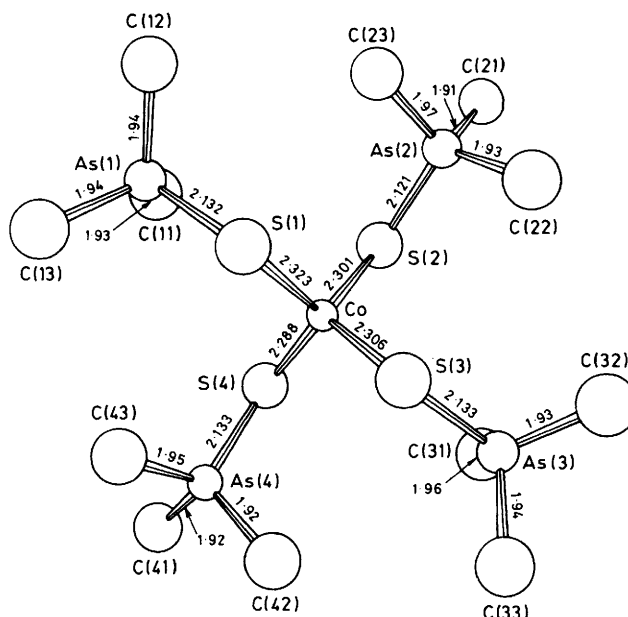


Figure 3. Cation of the green isomer viewed along the X direction in Figure 1(a). E.s.d.s for bond lengths: Co-S, 0.008; As-S, 0.008; As-C, 0.03 Å

reference). On the other hand the cation of the green isomer has a symmetry approximating C_{2v} (about the X axis of the cube, Figure 3). The relevant S-Co-S-As torsion angles (footnote d Table 2) are all nearly 180°, and the AsC₃ groups are in mirror-image relationship. The four sulphur atoms define a tetragonal spenoid with the point group D_{2d} and the S₄ symmetry extends to the CoS₄As₄ unit.

There remains the question as to whether the C_{2v} symmetry and 90° valence angles of the cation of the green isomer may have particular significance. Displacement of S(1), S(2), S(3), and S(4) to give bond directions through A, B, C, and D at the midpoints of the cube edges (Figure 1) provides the simplest description of the CoS₄ array.* It seemed a possibility that these midpoints between the two conjugate tetrahedral positions might correspond to a localised shallow energy trough from electronic effects, even though perhaps too small to be reflected in the experimentally determined Co-S bond lengths. For the spenoidal configuration the ligand field gives two degenerate higher-energy d orbitals well separated from the lower group [Figure 1 (b)]. Any field effect should therefore become more important for high-spin d⁸ complexes, since there would then be the maximum number of electrons in the three lower-energy orbitals.

The compounds [Ni(Me₃AsS)₄][ClO₄]₂ and [Ni(Me₃-AsS)₄][BF₄]₂ proved to be isomorphous with the green cobalt isomer, but neither nickel compound could be obtained in more than one crystalline form. The nickel compounds thus show a decisive preference for the 90°/120° spenoidal configuration. The strict isomorphism of these particular cobalt and nickel compounds is unlikely to be fortuitous, because, in the series [M(Me₃AsS)₄]X₂, with M = Fe, Co, Ni, or Zn and

* In the alternative description of the tetragonal spenoidal configuration in terms of angle spreading and counter rotation, the points S(1'), S(2'), S(3'), S(4') would lie on face diagonals, with coordinates -1, -y, y, etc. For the valence angles S(1')-Co-S(3') (θ) and S(1')-Co-S(2') (φ) there are the relationships cos θ = (1 - 2y²)/(1 + 2y²) and cos φ = -1/(1 + 2y²). For the 90°/120° spenoid, y = 1/√2 and the points are produced by a 45° anticlockwise rotation of A, B, C, and D about the X axis.

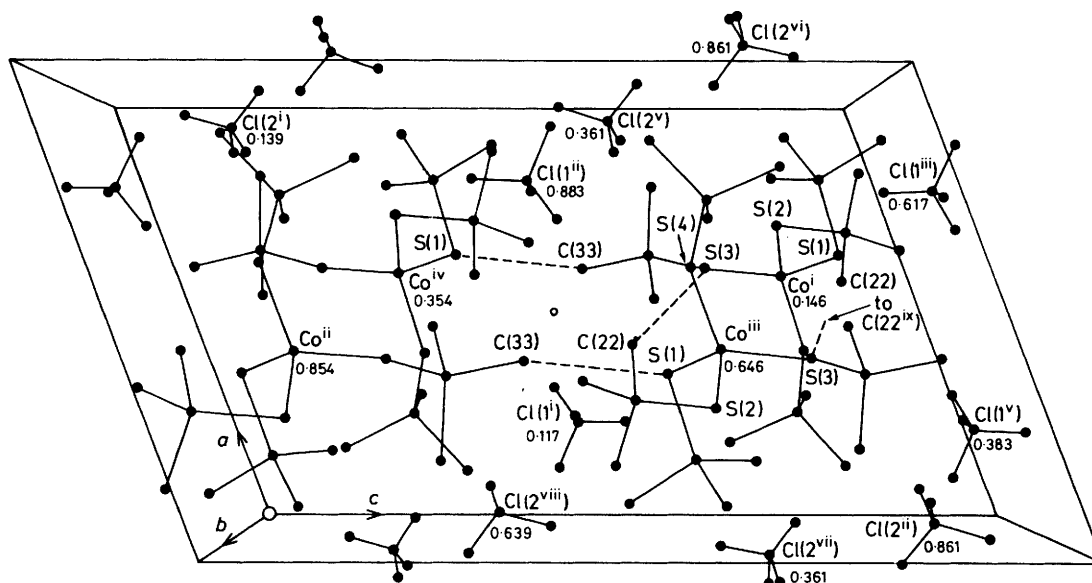


Figure 4. Unit cell of the blue isomer viewed down the y axis, showing y co-ordinates. i x, y, z ; ii $1 - x, 1 - y, 1 - z$; iii $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; iv $x, \frac{1}{2} - y, z - \frac{1}{2}$; v $x, \frac{1}{2} - y, \frac{1}{2} + z$; vi $2 - x, 1 - y, 1 - z$; vii $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$; viii $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; ix $x, 1 + y, z$

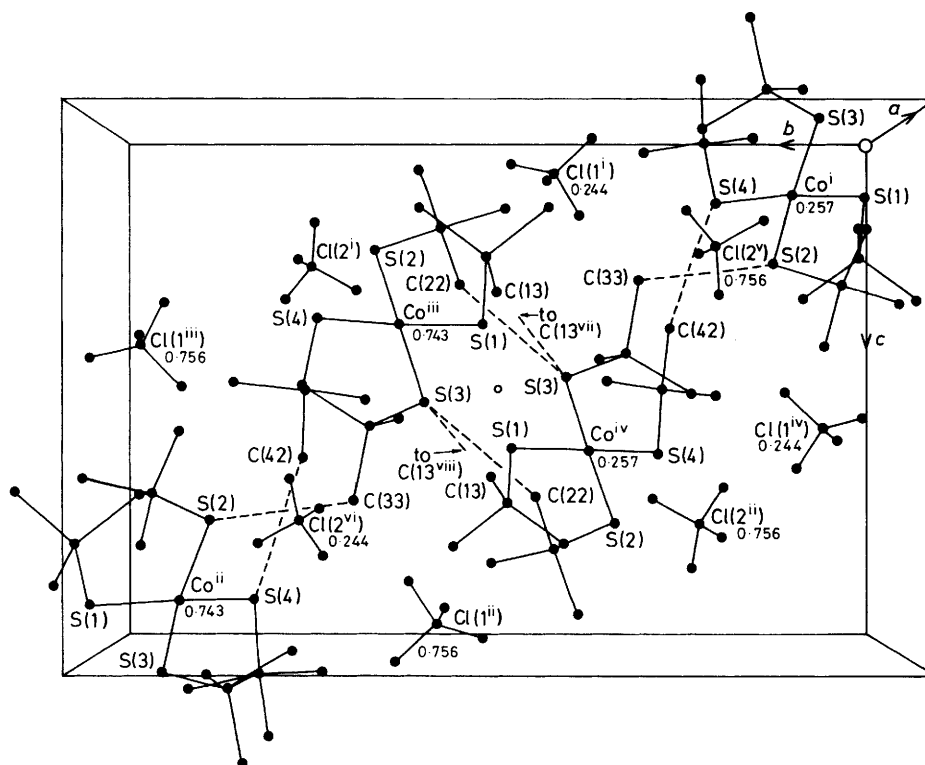


Figure 5. Unit cell of the green isomer viewed down the x axis, showing x co-ordinates. i x, y, z ; ii $1 - x, 1 - y, 1 - z$; iii $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; iv $x, \frac{1}{2} - y, \frac{1}{2} + z$; v $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; vi $x, \frac{3}{2} - y, \frac{1}{2} + z$; vii $-x, \frac{1}{2} + y, \frac{1}{2} - z$; viii $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$

$X = \text{ClO}_4^-$ or BF_4^- , isomorphism is not common, having been established only for the pair $[\text{Co}(\text{Me}_3\text{AsS})_4][\text{BF}_4]_2$ and $[\text{Zn}(\text{Me}_3\text{AsS})_4][\text{ClO}_4]_2$. It is therefore suggested that, although any ligand-field stabilisation must be weaker for d^7 cobalt than for d^8 nickel, its effect contributes specifically to the development of the $90^\circ/120^\circ$ valence angles shown by the green cobalt isomer. It is a possibility too that 'midpoint' stabilisation

could be enhanced through maximisation of the use of different σ -bonding (d_{xz} vs. d_{xy}) and π -bonding (d_{z^2} vs. $d_{x^2-y^2}$) orbitals when the ligands are in these mid-directions. Several cobalt thiourea complexes also show a tendency towards a pair of 90° valence angles⁴⁻⁶ but there is a variability, probably arising from cation-anion hydrogen bonding or the effects of nitrogen substituents.

Crystal Structures.—Crystals of both isomers are monoclinic, with the space group $P2_1/c$. Views of the unit cells are shown in Figures 4 and 5. There are two crystallographically independent anion sets in each isomer. Cation-anion distances are large, the shortest Co...Cl distances being: *blue* isomer, Co...Cl(1) 6.64(1) and Co...Cl(2) 6.59(1); *green* isomer, Co...Cl(1) 6.24(1) and Co...Cl(2) 6.44(1) Å. The packing within the crystals is determined by the particular distribution of the weak cation field with the charge dispersed over the AsMe₃ groups, and the sulphur atoms probably slightly negative. This permits the cations to stack in columns with the AsMe₃ groups pointing outwards towards the surrounding anions. However, the column formation differs in the two isomers.

In the blue isomer the cation columns extend parallel with the y -axis, along which the unit cell is viewed in Figure 4. Adjacent cations within each column, e.g. those centred on Coⁱ and Coⁱⁱⁱ, are in screw-axis relationship, with their cobalt y crystallographic co-ordinates differing by 0.5. The column containing Coⁱ and Coⁱⁱⁱ is surrounded by eight rows of anions passing through Cl(1ⁱ), Cl(1ⁱⁱⁱ), Cl(1^{iv}), and Cl(2ⁱⁱ), Cl(2^v), Cl(2^{vi}), Cl(2^{vii}). The individual cations in this column, if viewed as in Figure 2, would all have a right-handed swastika array of ligands (as shown), while the ligands in the corresponding column to the left of the cell form left-handed swastikas. In the green isomer the cations are arranged stepwise in pairs of side-by-side columns, extending parallel with the x axis of the cell (e.g. the pair passing through Coⁱⁱⁱ and Co^{iv} in Figure 5). As between the paired columns, the cations are centrosymmetrically related. The eight surrounding anion rows passing through Cl(1^{i-iv}) and Cl(2^{i,iii,v,vi}) enclose the pair of cation columns. In both structures a few intercation CH₃...S approaches at 3.6–3.7 Å (shown by broken lines in Figures 4 and 5) are less than the sum of the van der Waals radii, 3.85 Å, but their effects on isomer stability must be small.

The anions are loosely enclosed by irregular arrangements of methyl groups and show large thermal parameters, possibly indicating disorder. The numbers of methyl groups giving CH₃...Cl distances 3.9–4.5 Å are: *blue* isomer, Cl(1), nine methyl groups from six different arsenic atoms and five different cations; Cl(2), 6, 4, 3 respectively; *green* isomer, Cl(1), 10, 6, 5; Cl(2), 7, 4, 4. For all four anion types the calculated Cl–O bond lengths (averaging 1.26–1.38 Å) are not reliable and fall below accepted values, 1.427–1.441(4) Å,⁹ through the known computational effect which causes an apparent decrease in Cl–O length with increasing anisotropic thermal motion.¹⁰ Calculated CH₃...O distances, in relation to the corresponding CH₃...Cl values, are determined also by Cl–O orientation, but the CH₃...O distances cluster at 3.35–3.7 Å, with lower values of 3.25, 3.20, 3.16, and 2.95 Å. The range shows that the already weak ionic attractions grade into van der Waals contacts.

Compared with the As–S bond length in the free ligand, 2.057(3) Å,¹¹ the average value in the complexes is 2.13(1) Å. This would correspond to a decrease in bond order from 1.94 to 1.5,¹² or from 2.1 to 1.5 if based on the lengths of single and double As–S bonds given by Camerman and Trotter.¹³ There is a small statistical decrease in the S–As–C angle upon co-ordination, from 113.4(4) to 111.4(9)° (av.), and although crystal forces might have slightly modified the latter angle, this is compatible with charge withdrawal from the As–S bond. The sulphur bond angles (109.2°, av.) are similar to values reported for phosphine sulphide¹⁴ and thiourea^{4–6} complexes.

Experimental

Preparation of Complexes.—The cobalt isomers were obtained from cobalt(II) perchlorate hexahydrate and trimethylarsine sulphide (L) in stoichiometric proportions. Using

Table 3. Trimethylarsine sulphide complexes; analyses and $\nu(\text{M–S})$ i.r. bands

Compound ^a	Analysis (%) ^b		$\tilde{\nu}(\text{M–S})/\text{cm}^{-1}$
	C	H	
[CoL ₄][ClO ₄] ₂ (blue isomer)	16.8 (16.6)	4.1 ^c (4.2)	315ws, 295s
[CoL ₄][ClO ₄] ₂ (green isomer)*	16.3 (16.6)	4.4 (4.2)	337s, 312(sh), 290vs, 280s
[CoL ₄][BF ₄] ₂ † (green)	17.4 (17.4)	4.3 (4.3)	307s, 300(sh), 287s
[CoL ₄][PF ₆] ₂ (blue-green)	15.1 (15.05)	3.8 (3.8)	319s, 303s,br
[CoL ₄][BPh ₄] ₂ (blue-green)	32.8 (33.1)	8.5 (8.3)	307s, 300(sh), 287s
[NiL ₄][ClO ₄] ₂ * (green)	17.2 (16.6)	4.5 ^d (4.2)	346m, 322(sh), 285s, 277s
[NiL ₄][BF ₄] ₂ * (dark green)	17.3 (17.1)	4.5 (4.3)	344s, 325(sh), 285s, 276s
[ZnL ₄][ClO ₄] ₂ † (white)	16.9 (16.5)	4.2 (4.1)	287m, 277(sh)

^a The only cobalt nitrate obtainable was of composition CoL₂(NO₃)₂. The asterisks and daggers indicate isomorphous compounds. ^b Calculated values in parentheses. ^c Co, 6.7(6.8)%. ^d Ni, 6.7(6.8)%.

solutions in hot or cold ethanol, crystals of the blue isomer separated. With cold acetone, acicular crystals of the green isomer formed preferentially, but a few blue crystals also formed on the bottom of the vessel. Magnetic moments were measured by the Gouy method.

In searching for other isomers, and examples of isomorphism, (by X-ray powder photography), [CoL₄][BF₄]₂, [CoL₄][PF₆]₂, [CoL₄][BPh₄]₂, [NiL₄][ClO₄]₂, [NiL₄][BF₄]₂, and [ZnL₄][ClO₄]₂ were also prepared, using acetone and ethanol (Table 3). The hexafluorophosphate and tetraphenylborate were obtained through anion exchange using ammonium hexafluorophosphate and sodium tetraphenylborate. The isomorphous compounds [CoL₄][ClO₄]₂ (green), [NiL₄][ClO₄]₂, and [NiL₄][BF₄]₂ give similar $\nu(\text{M–S})$ bands (Table 3). The $\nu(\text{M–S})$ bands of [CoL₄][BF₄]₂, [CoL₄][PF₆]₂, [CoL₄][BPh₄]₂, and [ZnL₄][ClO₄]₂ generally relate more closely to the spectrum of the blue isomer.

Crystallography.—**Crystal data.** Blue isomer, C₁₂H₃₆As₄Cl₂CoO₈S₄, $M = 866.1$, monoclinic, $a = 11.730(2)$, $b = 14.810(2)$, $c = 20.024(3)$ Å, $\beta = 110.65(2)^\circ$, $U = 3\,255(1)$ Å³, $D_m = 1.79$ g cm⁻³, $Z = 4$, $D_c = 1.77$ g cm⁻³, $F(000) = 1\,716$, $\mu(\text{Mo–K}_\alpha) = 52.4$ cm⁻¹, space group $P2_1/c$.

Green isomer (where different), $a = 11.619(2)$, $b = 20.593(2)$, $c = 13.450(3)$ Å, $\beta = 93.23(2)^\circ$, $U = 3\,213(1)$ Å³, $D_m = 1.79$, $D_c = 1.79$ g cm⁻³, $\mu(\text{Mo–K}_\alpha) = 53.1$ cm⁻¹.

X-Ray data collection. The crystal systems and space groups were determined unambiguously from the Laue symmetry and systematic absences observed in precession photographs. Intensities were recorded at 20 °C on an Hilger and Watts four-circle diffractometer with Mo–K_α radiation, using the θ – 2θ scan technique. Twelve accurately centred reflections were used to determine unit-cell parameters and orientations. No intensity variations were observed for three standard reflections during the data collection on either isomer. Corrections for absorption and isotropic extinction were applied. For the blue isomer: crystal dimensions, $0.2 \times 0.07 \times 0.025$ mm; 2θ (max.) = 36° ; independent reflections, 2 239; reflections used [$I > 3\sigma(I)$], 1 178. For the green isomer: dimensions, $0.24 \times 0.038 \times 0.04$ mm; 2θ (max.) = 46° ; reflections, 2 002 and 1 225. In both cases the data and therefore the accuracy were limited by the small crystal sizes.

Table 4. Fractional atomic co-ordinates, with estimated standard deviations (e.s.d.s) in parentheses

Atom	Blue isomer			Green isomer		
	x	y	z	x	y	z
Co	0.584 6(4)	0.145 5(3)	0.818 2(2)	0.256 8(3)	0.116 7(2)	0.119 3(3)
As(1)	0.807 7(3)	0.312 6(3)	0.902 4(2)	0.042 8(3)	0.012 1(2)	0.231 6(2)
As(2)	0.699 0(3)	-0.035 5(3)	0.941 5(2)	0.479 8(3)	0.069 7(2)	0.302 5(2)
As(3)	0.634 9(3)	0.104 9(2)	0.653 4(2)	0.463 0(3)	0.160 5(2)	-0.067 5(2)
As(4)	0.261 7(3)	0.179 1(2)	0.769 3(2)	0.039 7(3)	0.221 7(1)	-0.000 2(2)
S(1)	0.632 0(8)	0.265 0(6)	0.896 9(5)	0.162 4(7)	0.017 2(4)	0.117 4(6)
S(2)	0.714 3(8)	0.022 7(6)	0.847 2(5)	0.368 1(7)	0.147 2(4)	0.258 3(6)
S(3)	0.601 1(8)	0.209 0(6)	0.718 3(4)	0.344 2(7)	0.088 3(4)	-0.024 1(6)
S(4)	0.403 0(9)	0.084 1(7)	0.815 3(5)	0.154 5(7)	0.211 3(4)	0.128 2(5)
C(11)	0.911(4)	0.221(3)	0.886(2)	0.043(3)	0.088(2)	0.316(2)
C(12)	0.803(4)	0.403(3)	0.836(2)	0.080(3)	-0.061(1)	0.318(2)
C(13)	0.894(4)	0.361(3)	0.998(2)	-0.109(3)	0.002(2)	0.166(2)
C(21)	0.655(3)	0.049(2)	0.999(2)	0.570(2)	0.097(1)	0.419(2)
C(22)	0.578(4)	-0.127(3)	0.918(2)	0.585(3)	0.047(2)	0.201(2)
C(23)	0.849(3)	-0.088(3)	0.996(2)	0.395(3)	-0.010(1)	0.334(2)
C(31)	0.532(3)	0.004(2)	0.643(2)	0.460(3)	0.242(1)	0.008(2)
C(32)	0.801(3)	0.061(2)	0.692(2)	0.618(3)	0.126(2)	-0.054(2)
C(33)	0.601(3)	0.154(2)	0.558(2)	0.435(3)	0.179(2)	-0.208(2)
C(41)	0.305(4)	0.296(3)	0.782(2)	-0.052(3)	0.299(1)	0.013(2)
C(42)	0.135(5)	0.168(3)	0.809(3)	0.120(3)	0.228(2)	-0.121(2)
C(43)	0.187(5)	0.155(3)	0.666(3)	-0.066(3)	0.149(2)	-0.017(2)
Cl(1)	0.235(2)	0.117(1)	0.476(1)	0.244(1)	0.424(1)	0.079(1)
Cl(2)	0.933(2)	0.139(1)	0.158(1)	0.245(1)	0.739(1)	0.258(1)
O(11)	0.125(3)	0.105(3)	0.426(2)	0.360(3)	0.434(2)	0.098(3)
O(12)	0.315(3)	0.069(3)	0.460(2)	0.199(3)	0.392(2)	0.156(3)
O(13)	0.232(5)	0.090(5)	0.538(2)	0.231(4)	0.376(2)	0.006(3)
O(14)	0.251(7)	0.202(3)	0.476(3)	0.180(3)	0.480(2)	0.055(3)
O(21)	0.883(5)	0.064(3)	0.161(2)	0.309(3)	0.732(2)	0.175(3)
O(22)	0.870(5)	0.207(4)	0.155(3)	0.142(4)	0.762(2)	0.240(2)
O(23)	1.022(5)	0.154(4)	0.214(3)	0.302(3)	0.772(4)	0.323(4)
O(24)	0.965(5)	0.135(3)	0.103(3)	0.231(7)	0.683(3)	0.303(5)

Structure solution and refinement. The structures were solved using direct methods. The E maps clearly showed the positions of the cobalt, arsenic, and sulphur atoms. Their co-ordinates were refined using isotropic thermal parameters. Subsequent electron-density syntheses revealed the remaining (non-hydrogen) atoms. Least-squares refinements were continued with the use of anisotropic thermal parameters for the atoms of the perchlorate ions. Hydrogen atoms were not located and were not introduced. For the blue isomer, refinement converged with $R = 0.066$ and $R' = 0.074$, for the green isomer, $R = 0.060$ and $R' = 0.069$. The function minimised was $\sum w|F_o| - |F_c|^2$, where the weights, w , were $4|F_o|^2/(\sigma|F_o|)^2$. Final Fourier difference calculations showed residual peaks not more than half the height at which the last (oxygen) atoms were located. Ratios of maximum least-squares shifts to error fell to <0.3 . Programs used in structure solution and refinement included locally modified versions of FORDAP and ORFLS.¹⁵ The SHELXTL package was used for display and plotting of structures. Atomic scattering factors were taken from ref. 16. Atomic co-ordinates are given in Table 4.

Acknowledgements

The authors acknowledge assistance towards provision of equipment from the New Zealand Universities Research Committee.

References

- 1 A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc. A*, 1968, 987.
- 2 A. M. Brodie, J. E. Douglas, and C. J. Wilkins, *J. Chem. Soc. A*, 1969, 1931.
- 3 C. D. Flint and M. Goodgame, *J. Chem. Soc. A*, 1967, 1718.
- 4 W. A. Spofford, P. Boldrini, E. L. Amma, P. Carfagno, and P. S. Gentile, *Chem. Commun.*, 1970, 40; W. A. Spofford and E. L. Amma, *J. Cryst. Mol. Struct.*, 1976, 6, 235.
- 5 R. F. Baggio, C. Manzanarez, and S. Baggio, *Acta Crystallogr., Sect. B*, 1975, 31, 2359.
- 6 T. G. Fawcett, E. E. Fehskens, J. A. Potenza, H. J. Schugar, and R. A. Lalancette, *Acta Crystallogr., Sect. B*, 1979, 35, 1460.
- 7 R. Karama, J. P. Declercq, G. Germain, and M. van Meerssche, *Bull. Soc. Chim. Belg.*, 1982, 91, 171.
- 8 R. L. Carlin, *Transition Met. Chem.*, 1965, 1, 1.
- 9 G. B. Johansson and O. Lindqvist, *Acta Crystallogr., Sect. B*, 1977, 33, 2918.
- 10 B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc. A*, 1969, 2407.
- 11 C. J. Wilkins, K. Hagen, L. Hedberg, A. Shen, and K. Hedberg, *J. Am. Chem. Soc.*, 1975, 97, 6352.
- 12 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1969, p. 239.
- 13 N. Camerman and J. Trotter, *J. Chem. Soc.*, 1964, 219.
- 14 P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 1971, 105.
- 15 G. M. Sheldrick, SHELXTL (version 4), Nicolet XRD Corp., Madison, Wisconsin, 1984; W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, ORNL-TM-306, Oak Ridge National Laboratory, Tennessee, 1964; A. Zalkin, FORDAP, personal communication.
- 16 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, 24, 321.