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Bis(ethylenediamine)(2-selenoacetato-*O*,*Se*)cobalt(III) Perchlorate

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Abstract. $[Co(C_2H_8N_2)_2(C_2H_2O_2Se)]ClO_4$, $P2_1/n$, a = 11·183 (2), b = 10·171 (2), c = 12·168 (3) Å, β = 96·22 (2)°, U = 1375·9 Å^3, Z = 4, μ(Mo $K\alpha$) = 4·33 mm^{-1}. The structure contains octahedral Co^{III} complex cations and perchlorate anions. The Co coordination is effected by four N atoms from the ethylenediamine ligands and O and Se atoms of the 2-selenoacetic acid ligand. The Co—N bond length for N *trans* to Se is 2·006 (7) Å whereas the mean for the three Co—N bonds *cis* to Se is 1·966 (7) Å, yielding a structural *trans* effect for the selenolato ligand in this complex of 0·040 (10) Å. This value is similar to that previously found for thiolato ligands in analogous Co^{III} complexes. The anisotropic thermal parameters for the perchlorate O atoms indicate that this ion undergoes significant librational motion or is rotationally disordered in the crystal. The structure was refined to an R of 0·046 for 1551 independent observed reflections.

Introduction. The structure of $[(en)_2Co(SeCH_2CO_2)]ClO_4$ has been determined as part of our program concerned with the structural *trans* effect in Co^{III} complexes (Elder, Heeg, Payne, Trkula & Deutsch, 1978). Specifically we wished to check our earlier observation that Se appears to cause a larger *trans* effect than S in such complexes (Stein, Ellis, Elder & Deutsch, 1976).

The synthesis and recrystallization of the title compound has been given elsewhere (Stein *et al.*, 1976). Preliminary precession photographs indicated the monoclinic space group $P2_1/n$. A lath-like brown-red crystal (0·06 × 0·11 × 0·72 mm) was mounted on a glass fiber with the long dimension coincident with the fiber axis. Intensity data were measured for 2354 reflections (3 < 2θ < 47°) using Mo $K\alpha$ radiation on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator. From these, 1551 unique, observed reflections [$I > 2\sigma(I)$] were obtained by averaging after application of analytical absorption corrections. Calculated transmission coefficients ranged from 0·50 to 0·76.

The non-hydrogen atoms were located from Patterson and electron density syntheses, H atoms were placed at calculated positions and given fixed isotropic temperature parameters (U = 0·05 Å^2). Refinement of non-hydrogen positional and anisotropic thermal parameters and H positional parameters converged to R = 0·046 and $R' = [\sum w\Delta^2/\sum w(F_o)^2]^{1/2}$ = 0·039. The unweighted residual for all reflections was 0·048. Refinement of H positional parameters resulted in significant (0·005 level) improvement of the model (Hamilton, 1965). Mean values of $w\Delta^2$ varied only slightly with $\sin\theta$ or $|F_o|$. A final difference map was essentially featureless, the highest peaks (0·7 e Å^{-3}) occurring in the vicinity of the perchlorate anion. Complex neutral-atom scattering factors were used. Final non-hydrogen atomic coordinates are given in Table 1, with bond lengths and angles in Tables 2 and 3.*

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* Lists of structure factors, anisotropic thermal parameters, H coordinates and H bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33914 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. The structure of the Co^{III} complex cation is shown in Fig. 1. Two features of the coordination geometry are worthy of note. First, the Co—N(2) bond [2·006 (7) Å] which is *trans* to Se is 0·040 (10) Å longer than the average of the three other Co—N bonds [1·966 (7) Å]. We have previously observed a *trans* effect of 0·063 (9) Å for $[(en)_2Co(SeCH_2CH_2NH_2)](NO_3)_2$ (Stein *et al.*, 1976) in reasonable agreement with the value found here.

Fig. 1 shows anisotropy of N(2) with the largest displacement nearly parallel to the Co—N(2) and N(2)—C(2) bonds, and Table 2 indicates that the N(2)—C(2) bond at 1·512 (10) Å is somewhat longer than the average of the other three N—C bonds, 1·481 (4) Å. Both this lengthening of the N(2)—C(2) bond, 0·031 (11) Å, and the direction of anisotropy may indicate a slight mispositioning of N(2). If N(2) were actually located closer to C(2), thus decreasing the N(2)—C(2) bond length, then the Co—N(2) distance would increase resulting in better agreement with the *trans* elongation found in our previous Co selenolato structure. However, for thiolato ligands in analogous complexes, we have observed *trans* effects of 0·040 (10) Å (Elder, Florian, Lake & Yacynych, 1973). Thus the available data do not permit a clear distinction to be made between the structural *trans* effects caused by thiolato and selenolato ligands in Co^{III} amine complexes.

Table 1. *Atom coordinates* ($\times 10^4$)

	x	*y*	*z*
Co	2695 (1)	1523 (1)	1408 (1)
Se	4332 (1)	119 (1)	1932 (1)
Cl	2130 (2)	1133 (2)	5630 (2)
O(1)	4782 (4)	3403 (5)	3810 (4)
O(2)	3367 (4)	2735 (4)	2523 (3)
O(3)	2753 (12)	292 (8)	4992 (6)
O(4)	2667 (7)	1034 (9)	6692 (5)
O(5)	2185 (11)	2360 (7)	5189 (7)
O(6)	998 (8)	650 (12)	5555 (10)
N(1)	1773 (5)	689 (5)	2501 (4)
N(2)	1248 (6)	2689 (7)	1119 (4)
N(3)	2042 (7)	359 (6)	207 (5)
N(4)	3572 (6)	2358 (6)	267 (5)
C(1)	661 (7)	1422 (8)	2651 (6)
C(2)	203 (6)	2000 (7)	1565 (6)
C(3)	2780 (7)	457 (8)	−728 (6)
C(4)	3102 (7)	1865 (7)	−846 (5)
C(5)	5116 (9)	1408 (9)	2955 (9)
C(6)	4383 (6)	2564 (6)	3133 (5)

Table 2. *Bond lengths* (Å)

Co—Se	2·355 (1)	N(1)—C(1)	1·478 (10)
Co—O(2)	1·924 (4)	N(2)—C(2)	1·512 (10)
Co—N(1)	1·962 (6)	N(3)—C(3)	1·479 (11)
Co—N(2)	2·006 (7)	N(4)—C(4)	1·486 (9)
Co—N(3)	1·960 (6)	C(1)—C(2)	1·486 (10)
Co—N(4)	1·977 (7)	C(3)—C(4)	1·487 (11)
Cl—O(3)	1·392 (10)	C(5)—C(6)	1·463 (12)
Cl—O(4)	1·367 (6)	Se—C(5)	1·949 (10)
Cl—O(5)	1·362 (8)	O(1)—C(6)	1·236 (8)
Cl—O(6)	1·351 (10)	O(2)—C(6)	1·300 (7)

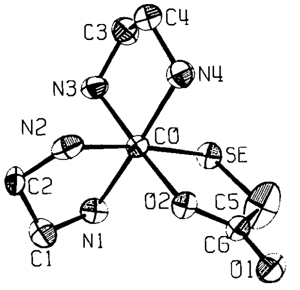

Fig. 1. The complex Co^{III} cation with H atoms omitted.

Table 3. *Bond angles* (°)

Se—Co—O(2)	88·0 (1)	Co—N(1)—C(1)	112·1 (4)
Se—Co—N(1)	90·3 (2)	Co—N(2)—C(2)	107·7 (4)
Se—Co—N(2)	174·0 (2)	Co—N(3)—C(3)	109·9 (5)
Se—Co—N(3)	92·9 (2)	Co—N(4)—C(4)	110·0 (5)
Se—Co—N(4)	91·2 (2)	Co—Se—C(5)	92·7 (3)
O(2)—Co—N(1)	89·6 (2)	Co—O(2)—C(6)	124·5 (4)
O(2)—Co—N(2)	89·5 (2)	N(1)—C(1)—C(2)	107·7 (6)
O(2)—Co—N(3)	176·6 (2)	N(2)—C(2)—C(1)	107·3 (5)
O(2)—Co—N(4)	92·0 (2)	N(3)—C(3)—C(4)	107·5 (6)
N(1)—Co—N(2)	84·3 (2)	N(4)—C(4)—C(3)	107·7 (6)
N(1)—Co—N(3)	93·7 (3)	Se—C(5)—C(6)	114·5 (6)
N(1)—Co—N(4)	177·9 (2)	O(2)—C(6)—C(5)	119·5 (6)
N(2)—Co—N(3)	89·9 (3)	O(2)—C(6)—O(1)	121·2 (6)
N(2)—Co—N(4)	94·3 (3)	O(1)—C(6)—C(5)	119·1 (7)
N(3)—Co—N(4)	84·8 (3)		
O(3)—Cl—O(4)	106·7 (5)	O(4)—Cl—O(5)	113·9 (6)
O(3)—Cl—O(5)	107·2 (6)	O(4)—Cl—O(6)	110·5 (6)
O(3)—Cl—O(6)	105·1 (7)	O(5)—Cl—O(6)	112·8 (7)

Secondly, the apparent anisotropy of C(5), shown in Fig. 1, may result from a disorder at that atom. This centrosymmetric crystal contains enantiomeric pairs of Λ and Δ isomers of the complex cation. The puckering of the ethylenediamine rings provides two additional chiral centers, giving rise to the $\Lambda(\lambda\delta)$ configuration illustrated. The dihedral angle about C(1)—C(2) is 49·3° and about C(3)—C(4) is 48·9°, whereas the angle about C(5)—C(6) is only 8·4° due to the carboxylate planarity. A slight (~0·3 Å) movement of C(5) to the other side of the mean selenoacetic acid ligand plane would result in accommodation of the diastereomer in the same site, *i.e.* the $\Lambda(\lambda\delta\delta')$ and $\Lambda(\lambda\delta\lambda')$ diastereomers could both occupy the site depicted.

If the crystal contained equal numbers of each diastereomer, then this disorder would, at the first approximation, give rise to a planar Co—Se—C(5)—C(6)—O(2) ring. Since the ring is definitely, if slightly, puckered we must conclude that there is some preference for the particular diastereomer shown. All interionic contacts appear quite normal for complexes of this type.

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Structure du Bis(thiocyanato)(triphénylphosphine)mercure(II)

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Abstract. $Hg[P(C_6H_5)_3](SCN)_2$, $C_{20}H_{15}HgN_2PS_2$, monoclinic, $P2_1/c$, $a = 10{\cdot}075\ (6)$, $b = 21{\cdot}136\ (11)$, $c = 10{\cdot}745\ (4)$ Å, $\beta = 112{\cdot}37\ (4)°$, $Z = 4$, $D_c = 1{\cdot}817$ Mg m^{-3}. The Hg atom has trigonal-planar coordination to two S-bonded thiocyanato groups and the P atom of the triphenylphosphine group. Two weaker Hg···N interactions with thiocyanate ligands in adjacent molecules complete a distorted trigonal bipyramid around the Hg atom. The steric effect of triphenylphosphine corresponds to a cone angle 5° greater than that of triphenylarsine in the isomorphous complex.

Introduction. Dans le cadre de nos travaux sur les complexes du mercure, nous avons étudié plusieurs composés renfermant le groupement SCN, notamment $Hg(SCN)_2.2tpP$ (où tpP = triphénylphosphine; Makhija, Beauchamp & Rivest, 1973) et $Hg(SCN)_2.tpAs$ (où tpAs = triphénylarsine; Hubert, Beauchamp & Rivest, 1975; Makhija, Beauchamp & Rivest, 1972). Récemment, d'autres chercheurs (Alyea, Dias, Ferguson & Restivo, 1977) ont entrepris l'étude de complexes formés par plusieurs sels de mercure avec des phosphines substituées, dans le but de préciser l'influence de l'encombrement stérique des coordinats.

La similitude des paramètres de maille et l'appartenance au même groupe spatial laissaient supposer que le composé $Hg(SCN)_2.tpP$ et son homologue $Hg(SCN)_2.tpAs$ sont isostructuraux. Nous avons donc entrepris l'étude cristallographique du complexe de la tpP, afin de comparer les effets stériques respectifs de ces deux coordinats dans des composés où les autres facteurs varient peu.

Les cristaux sont obtenus par évaporation d'une solution éthanolique renfermant des quantités équimoléculaires de tpP et de $Hg(SCN)_2$. Le travail cristallographique est effectué au moyen d'une plaquette mesurant 0,10 × 0,065 × 0,22 mm, perpendiculairement à {100}, {010} et {001} respectivement. Les extinctions systématiques notées sur une série de films de précession déterminent sans ambiguïté le groupe spatial $P2_1/c$. Les valeurs précises des paramètres de maille sont obtenues par affinement des coordonnées 2θ, ω et χ de 15 réflexions Mo $K\bar{\alpha}$ (λ = 0,71068 Å, monochromateur de graphite) centrées et indexées automatiquement sur un diffractomètre automatique Syntex $P\bar{1}$.

Les intensités des réflexions sont enregistrées avec le même instrument en effectuant un balayage $\theta/2\theta$ sur un intervalle allant de $[2\theta(K\alpha_1) - 1{,}0]°$ à $[2\theta(K\alpha_2) + 1{,}0]°$. La vitesse de balayage est de $1{,}0(2\theta)°$ min^{-1} pour la majorité des taches, mais des vitesses atteignant 24° min^{-1} sont choisies automatiquement par le programme d'enregistrement des données pour les réflexions les plus intenses. Une mesure du fond continu est effectuée aux extrémités de l'intervalle de balayage. Sa durée est ajustée de manière qu'il y ait un rapport de 0,4 entre la durée du comptage de fond continu et celle du pic. Les fluctuations d'intensité suivies à l'aide de trois témoins restent inférieures à ±4% pendant l'expérience.

Les réflexions hkl et $hk\bar{l}$ comprises dans la sphère $2\theta \leq 50°$ sont enregistrées. Après élimination des témoins, il reste un ensemble de 3755 réflexions indépendantes. L'intensité nette I est calculée selon l'équation $I = (I_t - B/0{,}40)S$ où I_t est l'intensité enregistrée durant le balayage, B est l'intensité du fond continu et S, la vitesse de balayage. L'écart-type $\sigma(I)$ est obtenu d'après $\sigma^2(I) = (I_t + B/0{,}16)S^2 + (0{,}04\ I)^2$. En posant la condition $I \geq 2{,}5\sigma(I)$, nous retenons

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