Synthesis, Stability, and *X*-Ray Structure of an *NS*-Bound *S*-Methyl(*R*)cysteine Complex of Cobalt(III)

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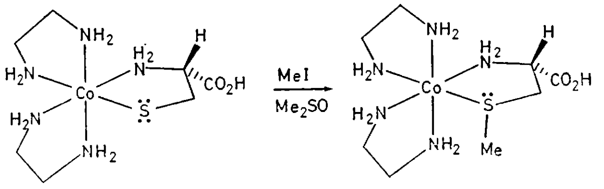
Summary The synthesis and *X*-ray crystal structure of Λ-*NS*-[Co(ethylenediamine)$_2$(*S*)*S*-methyl(*R*)cysteinato]-(NCS)$_2$ are described; sulphur bonding of the sulphide is established, the chiral *S*-methyl centre is stereospecifically oriented, and rearrangement from the *NS* to the *NO* bound isomer was not observed under acidic conditions.

A complex ion of the form [Co(en)$_2$(cysteinato)]$^{2+}$ (**1**),† where the cysteine residue is argued to be *NS* bound, has been described previously.[1] Methylation at the sulphur atom supposedly gave the unstable *S*-bonded sulphide complex (**2**) which then rapidly rearranged to the *NO* linkage isomer. Only the supposed *NO* form was isolated and the same complex was obtained by reaction of the sulphide ligand with Co(en)$_2$X$_2$ type complexes.[1]



(1) (2)

This note reports the synthesis, structure, and properties of the *S*-bound sulphide complex and shows that such chelated sulphide complexes are stable to rearrangement of the bonding atoms.

The complexes [Co(en)$_2$(*R*)(cysS)](ClO$_4$)$_n$ (n = 1 or 2)† have been synthesized in Λ and Δ forms and *X*-ray crystallographic studies[2] have shown that both isomers have cysteine bound through the N and S atoms. Either form and methyl iodide or methyl triflate (CH$_3$OSO$_2$CF$_3$) in dimethyl sulphoxide at 20 °C react to give a brown to orange colour change over a few minutes. Ion-exchange chromatography yielded only a single band of the *S*-methyl derivative [Co(en)$_2$(*R*)(cysSMe)]$^{3+}$ (**2**) which crystallized as the Cl$^-$, NCS$^-$, or I$^-$ salt in quantitative yield. The thiocyanate was obtained also as a deprotonated (at CO$_2$H) form [Co(en)$_2$(*R*)(cysSMe)](NCS)$_2$ or partly deprotonated double salt‡ [Co(en)$_2$(*R*)(cysSMe)](NCS)$_{2·5}$. Crystals of the former§ were more suitable for crystallography.

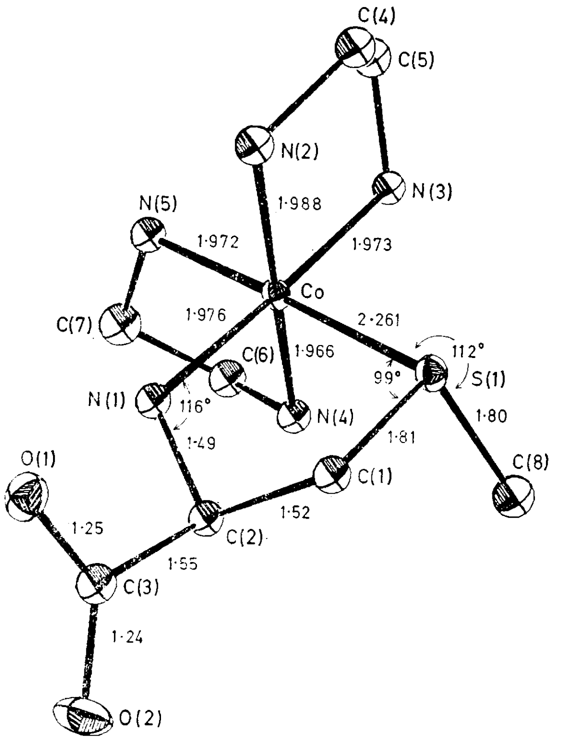


Figure. The molecular structure of *S*-methyl(*R*)cysteinatobis(ethylenediamine)cobalt(III) thiocyanate: Co(C$_4$H$_{16}$N$_4$)(C$_4$H$_8$NSO$_2$)(NCS)$_2$, orthorhombic, space group $P2_12_12_1$, a = 8·723(1), b = 24·753(3), c = 8·149(2) Å; U = 1759·8 Å^3, M = 429·5; D_m = 1·60(5); D_c = 1·60 g cm^{-3} for Z = 4; μ(Mo-K_α) = 13·7 cm^{-1}. Unique data with $\theta \leqslant$ 32·5° were collected on an automatic diffractometer. Full-matrix least-squares refinement using the 2447 reflections $I > 3\sigma(I)$ converged to R 0·044.

The structure (Figure)¶ shows the sulphide derived from the Λ(*R*)cysteinato complex (**1**) and the present work confirms Λ and *R* absolute configurations[2,3] about the cobalt ion and the methine carbon respectively. More importantly, the *S*-methylated ligand is still *NS* bound and this result is not consistent with the earlier publication which indicated that the *NO* isomer was obtained from a similar reaction to that which we describe here. Although

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† Abbreviations used: en = ethylenediamine; (*R*)cysS = (*R*)cysteinato = NH$_2$CH(CO$_2$H)CH$_2$S$^-$ or NH$_2$CH(CO$_2$$^-$)CH$_2S^-$; (*R*)cysSMe = NH$_2$CH(CO$_2$H)CH$_2$ SMe or NH$_2$CH(CO$_2$$^-$)CH$_2$SMe; dmso = dimethyl sulphoxide.

‡ Similar double salts are known for other *NS*-(*R*)cysteinato complexes and the unit cell contains -CO$_2$$^-$ groups from adjacent complex ions sharing a proton (*e.g.*, ref. 3).

§ Satisfactory elemental analyses were obtained; $[M]_{546}$ + 4260, $[M]_{436}$ − 6390, $[M]_{365}$ − 4590 deg l mol^{-1} m.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table, packing diagram, and table of close intermolecular contacts are available as Supplementary Publication No. Sup. 22610 (19 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I and II*, Index Issues.

we have not been able to duplicate the original work we cannot preclude a Co^{II} catalysed[3,4] *NS* to *NO* rearrangement similar to that seen in related Co^{III} sulphur chemistry.

For comparison the Λ-*NO*-$[Co(en)_2(R)(cysSMe)]^{2+}$ linkage isomer was independently synthesized by the reaction of *cis*-$[Co(en)_2(dmso)_2](ClO_4)_3$ and *S*-methyl(*R*)cysteinato ion in DMSO. The Λ and Δ diastereoisomers were readily separated by ion-exchange chromatography. We note that the Λ-*NS* isomer's visible spectrum is very similar to that of the *NO* isomer's for the first ligand field band (*NS*: ϵ_{485}^{max} 152; *NO*: ϵ_{486}^{max} 89·5 l mol^{-1} cm^{-1}; H_2O) except that the *NS* isomer's molar absorptivity is larger. The second ligand field band, clearly observed for the *NO* isomer (ϵ_{336}^{max} 128), is obscured by a charge transfer band in the *NS* isomer's spectrum and this is characteristic of *S*-bonding to the metal ion.[2-4] In the light of these results, the data of Kothari and Busch[1] indicate that they obtained, as claimed, only the *NO* form, the ^1H n.m.r. spectrum of which revealed a mixture of $\Lambda(R)$ and $\Delta(R)$ diastereoisomers.

The bound sulphide is also chiral at sulphur and two further diastereoisomers might be expected from this source. The isomer found in the crystal had chirality *S* at the sulphur centre and a solution of the same ion showed only evidence for a chromatographically homogeneous product. Also, the batch of crystals were crystallographically homogeneous. These factors point to a stereospecific formation of one epimer or a rapid interconversion between the two. Related studies for the analogous tris(2-aminoethyl)amine (tren) complexes $[Co(tren)(R)(cysSMe)]^{n+}$ (n = 2,3) indicate that *S*-inversion is slow on the n.m.r. time scale[4] ($10 > k > 0{\cdot}1\ s^{-1}$; 30 °C). It should be noted that the present $\Lambda(R)$ and $\Delta(R)$ sulphides each showed evidence of only one isomer in both their ^1H and ^{13}C n.m.r. spectra. These results imply that, under equilibrium conditions, the *S*-methyl group is stereospecifically oriented, and for the $\Lambda(R)$ isomer the sulphur configuration is probably that found in the solid state (Figure). This orientation, where the *S*-methyl is axial and disposed between the en chelates, and where the five-membered ring is λ with an equatorial carboxylate group, is exactly analogous to that found[3] for the oxygen attached to sulphur in Λ-*NS*-$[Co(en)_2(R)(cys(S)SO)]^+$. In the latter case this is the established and preferred orientation and, unlike the present sulphide, the sulphur centre is stable to inversion.

Finally, acidic solutions of the sulphide complex (**2**) did not change significantly over at least 7 days at 25 °C (^1H and ^{13}C n.m.r., visible, and rotatory dispersion spectra) whereas decomposition was rapid in base (pH $\geqslant$ 10) or in hot neutral solution. In the latter case a multitude of products were obtained in small yield, amongst them the *NO* isomer and the chelated imine $[Co(en)_2(NH{=}CMeOCO)]^{2+}$.

These observations establish the inherent thermal stability of the *S*-bound sulphide as a ligand in dilute acid but in line with other observations[2-4] indicate that such Co–S complexes are susceptible to rearrangements induced by base and/or Co^{II}.

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[1] V. M. Kothari and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 2276.
[2] H. C. Freeman, C. J. Moore, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 3513.
[3] W. G. Jackson, A. M. Sargeson, and P. O. Whimp, *J.C.S. Chem. Comm.*, 1976, 934.
[4] W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 2165.