Reduction of a Cobalt(III) Sulphenamide Complex to (*R*)-Cysteine and (*RR*)-Cystine Complexes. *X*-Ray Crystal Structure of the Cystine Dimer

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Summary The synthesis of an *NO* bound cysteine complex of cobalt(III) and the *X*-ray crystal structure of a dimer form obtained *en route* are described.

NS-Bound (*R*)-cysteine in Δ- and Λ-(*R*)-cysteinato-bis(ethylenediamine)cobalt(III) ions (I) of known configuration[1] is oxidized in Me_2SO–Ac_2O and a remarkable transformation ensues to a sulphenamide (II) (Figure).[2] The cysteine entity has switched from *NS* to *NO* bonding and the sulphur atom has undergone a $2e^-$ oxidation and is finally captured in a stereospecific manner by deprotonated ethylenediamine (amide) ion. The mechanism of this rearrangement has been discussed previously.[2] We report (i) that a $2e^-$ reduction of the S atom in the sulphenamide regenerates thiol sulphur without reversing the *NO* bonding arrangement to *NS* and (ii) the structure of another complex which is also generated through the reduction process.†

A buffered (pH 7, 0·01 M, HPO_4^{2-}–$H_2PO_4^-$) aqueous solution of (II) is rapidly reduced by an excess of BH_4^- ion to give two orange products. Ion exchange chromatography indicated different ionic charges, 2+ and greater, and the isolated salts analysed for $[Co(en)_2(cysteinato)]^{2+}$ (en = ethylenediamine). A single crystal *X*-ray diffraction study has revealed the higher charged species to be the dimer (IV) (Figure) which exhibits the following features: (i) one cystinato-residue bridges two cobalt atoms, (ii) the linked cysteines chelate through the nitrogen and oxygen atoms, (iii) each half of the dimer, which possesses a crystallographic diad axis through the S–S bond, has Δ and *R* absolute configurations about cobalt and carbon, respectively, and (iv) the en rings of each cobalt adopt δ and λ conformations.

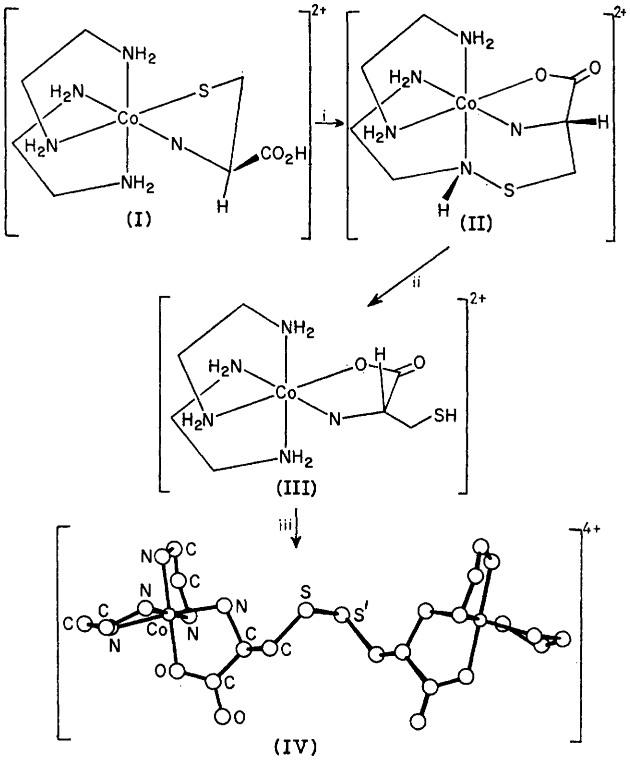

FIGURE. Reduction of sulphenamide to thiol and disulphide and the structure of the disulphide cation (IV): i, Me_2SO–Ac_2O at 20 °C; ii, $S_2O_4^{2-}$ or BH_4; iii, +(II). Crystals of the tetraperchlorate-6-hydrate, $C_{14}H_{54}Cl_4Co_2N_{10}O_{26}S_2$, are orthorhombic, space group $P2_12_12$ with $a = 35{\cdot}708(4)$, $b = 8{\cdot}869(1)$, $c = 6{\cdot}847(1)$ Å, $Z = 2$. Intensities were measured on a Picker FACS-1 diffractometer using Cu-K_α radiation and were corrected for absorption. Least-squares refinement gave an *R* of 0·073 for the 1996 reflexions (*hkl and $\bar{h}kl$*) with $I > 3\sigma(I)$ and $\theta < 60°$. Bond lengths are: Co–O, 1·899(6); Co–N, 1·932—1·961(8); and S–S′, 2·029(8) Å. ∠C–S–S′ is 102·9(5) and the dihedral ∠ C–S–S′-C is 98·2°.

We infer from this structural study and other evidence that the other product (III) (Figure) is the *NO* bound cysteine complex with a free thiol group. The visible spectra for the two ions (III) and (IV) are almost identical, showing two ligand field bands at 485 and 344 nm, characteristic of *NO* bound amino-acid chelates.[3] Furthermore, the o.r.d. curves for both ions are almost identical and are similar to a

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† 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.

variety of sulphur-free *NO*-[Co(en)$_2$(amino-acid)]$^{2+}$ complexes.[3] The absolute configurations deduced from these o.r.d. data are also consistent with the previously known and present structural results.

Clearly the BH$_4^-$ ion has cleaved the N–S linkage and presumably the monomeric thiol is the initial product. Formation of the dimer could arise either from aerial oxidation of (III) or by rapid attack of (III) on (II). These two proposals have been distinguished by experiment. The thiol complex was not oxidized ($<4\%$) in air over 4 days (pH 0—7) whereas the dimer formed very rapidly on mixing (III) and (II).

The free thiol (III) was methylated readily by MeI to produce the Δ-*NO*-[Co(en)$_2$-(*R*)-{NH$_2$CH(CH$_2$SMe)CO$_2$}]$^{2+}$ ion identical to that prepared by other routes. Compound (III) was oxidized back to (II) by Me$_2$SO–Ac$_2$O (Figure) but neither the methylated molecule nor the dimer (IV) undergo this oxidation. The observations confirm the presence of the free thiol and support the proposed mechanism[2] of the Me$_2$SO–Ac$_2$O oxidation of (I).

Similar observations have been made for the Λ form. Also, the $\Delta\Lambda$ dimer containing the (*R*)-cysteine residues was synthesised from Δ sulphenamide and Λ thiol and *vice versa*. The ^{13}C n.m.r. spectra clearly distinguish the mixed $\Delta\Lambda$ dimer from a 1 : 1 mixture of $\Delta\Delta$ and $\Lambda\Lambda$.

Dithionite reduction of (II) in neutral or slightly acidic solution gives largely (III) ($>80\%$). Two minor products were characterized as the perchlorate salt of (IV) and Δ-*NO*-[Co(en)$_2$-(*R*)-{NH$_2$CH(CH$_2$SSO$_2$)CO$_2$}]$^+$ dithionate. Presumably the reduction proceeds, in part, by direct attack of S$_2$O$_4^{2-}$ at the sulphenamide S atom with loss of SO$_2$ to give (III). The thiosulphonate shows little tendency to extrude SO$_2$ and give the thiol in acid solution.

The disulphide dimer was not reduced to the thiol by BH$_4^-$ or S$_2$O$_4^{2-}$. However, it was readily cleaved by CN$^-$ to give 50% (III), and 50% thiocyanato-complex Δ-*NO*-[Co(en)$_2$-(*R*)-{NH$_2$CH(CH$_2$SCN)CO$_2$}]$^{2+}$. The latter ion reacts further under the basic conditions and the structure of that product will be reported later.

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[1] W. G. Jackson, A. M. Sargeson, H. C. Freeman, and C. M. Moore, unpublished results.

[2] G. J. Gainsford, W. G. Jackson, and A. M. Sargeson, submitted to *J. Amer. Chem. Soc.*

[3] B. F. Anderson, D. A. Buckingham, G. J. Gainsford, G. B. Robertson, and A. M. Sargeson, *Inorg. Chem.*, 1975, **14**, 1658, and references therein.