Ring Expansion in a Metal–Dithiocarbamate Complex by Oxygen Insertion; Synthesis and Properties of $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$. The *X*-Ray Structure of Bis[*NN*-diethyl(dithiocarbamato-*SS*′)][*NN*-diethyl(dithioperoxycarbamato-*OS*)]chromium(III)

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Summary The synthesis and properties of the new complexes $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$ (R = Me or Et), in which one dithiocarbamate ligand has been oxidized to the hitherto unknown dithioperoxycarbamate ligand, are described; expansion of the chelate ring is confirmed from a single crystal *X*-ray structural analysis of the diethyl derivative.

THE oxidation by elemental sulphur of 1,1-dithiolate ligands when complexed to nickel(II) was first described by Coucouvanis and Fackler.[1] That the 'sulphur rich' products involved ring expansion to form a perthiodithiolate ligand was established by *X*-ray structural analysis of the $[Fe(p\text{-}MeC_6H_4SC_2)_2(p\text{-}MeC_6H_4CS_3)]$ complex.[2] This type of oxidation, in which sulphur inserts into an Fe–S bond with a concomitant expansion from a four- to a five-membered chelate ring, has only been observed for the addition of sulphur.

We report here the synthesis, properties, and structure of a new metal complex, $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$ in which an analogous ring expansion, involving oxygen rather than sulphur, has occurred.

Typically, the complexes were prepared from the reaction of $Na(S_2CNR_2)$ (R = Me or Et) with $K_2Cr_2O_7$ (mol ratio *ca.* 6 : 1) in aqueous solution. The green precipitate which formed immediately was filtered off, dried, and extracted into dichloromethane. Chromatography on silica with dichloromethane effected separation of $[Cr(S_2CNR_2)_3]$ and $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$ as the first two fractions. Evaporation of the solvent from the second fraction gave blue crystals of the title complex, the dimethyl derivative crystallising with one molecule of dichloromethane of solvation.†

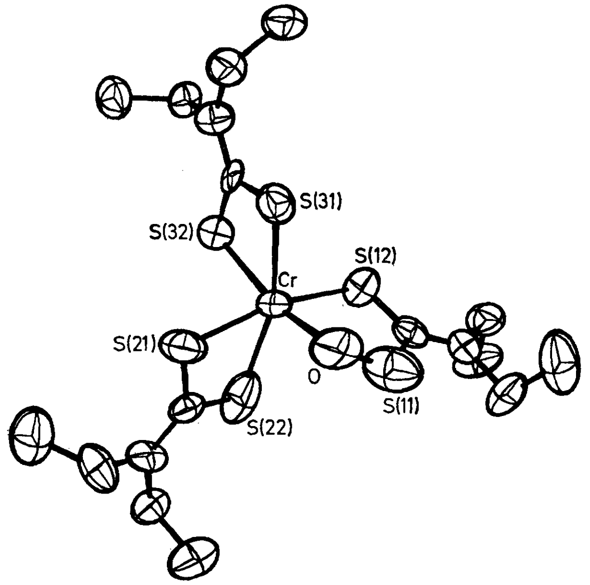

FIGURE. The molecular structure of $[Cr(S_2CNEt_2)_2(OS_2CNEt_2)]$. Principal bond lengths are Cr–O, 2·008(16); Cr–S(12), 2·392(7); Cr–S(21), 2·407(8); Cr–S(22), 2·433(8); Cr–S(31), 2·401(6); Cr–S(32), 2·399(6); S(11)–O, 1·263(21); C(1)–S(11), 1·721(21); and C(1)–S(12), 1·657(19) Å. The ellipsoids are drawn at the 50% probability level.

The mass spectra of both derivatives gave parent-ion peaks consistent with the formulation $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$ (R = Me, *m/e* 428; R = Et, *m/e* 512). The molecular weight of the diethyl derivative in solution (M = 513, in CH_2Cl_2 at 25 °C) accorded with a monomer. The effective magnetic moments (3·63 B.M., R = Me; 3·68 B.M., R = Et) are consistent with the d^3 Cr^{III} electronic configuration. This is confirmed by the close similarity of the electronic spectra (CH_2Cl_2 solution) with those of the corresponding tris-chelated complexes $[Cr(S_2CNR_2)_3]$, there being only slight shifts in both peak positions and intensities: $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$, λ/nm (log ϵ) R = Me, 670 (2·45), *ca.* 690(sh), and 490 (2·32); R = Et, 666 (2·49) and 492 (2·37); $[Cr(S_2CNR_2)_3]$, R = Me, 638 (2·47) and 491 (2·46); R = Et, 637 (2·59) and 494 (2·61). The i.r. spectrum (2000—200 cm^{-1}) of $[Cr(S_2CNMe_2)_2(OS_2CNMe_2)]$ is substantially similar to that of $[Cr(S_2CNMe_2)_3]$ with the appearance of extra bands at 1009(m), 885(m), 851(s), 560(w), 488(m), 418(w), and 382(w) cm^{-1}.‡ The new absorption at 1009 cm^{-1} is assigned as a ν(S–O) stretching vibration by analogy with ν(S–O) of 1025—985 cm^{-1} in metal complexes of dimethylsulphoxide.[3] Similarly the new band at 488 cm^{-1} can be assigned to a ν(Cr–O) vibration. Equivalent peaks in the spectrum of the diethyl derivative occur at 1015(sh), 1000(sh), and 486(m) cm^{-1}. This suggested that a dithiocarbamate ligand had undergone a novel oxidation *via* oxygen atom insertion into a Cr–S bond.

This conclusion was confirmed by a single crystal *X*-ray structural analysis of the diethyl derivative.

Crystal data: $C_{15}H_{30}CrN_3OS_6$, monoclinic, a = 17·939(5), b = 8·316(2), c = 16·195(7) Å, β = 96·65(3)°, space group $P2_1/c$, D_m = 1·42(1), D_c = 1·419 g cm^{-3} for Z = 4. Reflection data were collected on a Syntex-$P\bar{1}$ diffractometer using graphite crystal monochromated Mo-K_α radiation. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on 1530 reflections (corrected for absorption, μ = 9·8 cm^{-1}) with $I \geqslant 3\sigma(I)$ to a final R factor of 0·099 (non-hydrogen atoms anisotropic, methylene hydrogen atoms fixed position).§

The molecular structure of $[Cr(S_2CNEt_2)_2(OS_2CNEt_2)]$ (Figure) shows that the chromium atom is pseudo-octahedrally co-ordinated by two 'normal' dithiocarbamate ligands and by one dithioperoxycarbamate ligand. The unique ligand has been generated by oxygen atom addition at one sulphur atom resulting in chelate ring expansion to give an *OS*-bonded ligand.

The Cr–O distance, 2·01 Å, is a little longer than observed in other Cr^{III} complexes, *e.g.* $Cr(acac)_3$ (acacH = $MeCOCH_2COMe$), 1·95;[4] $Cr(glycine)_3$, 1·965;[5] and $Cr(oxalate)_3{}^{3-}$, 1·970 Å;[6] structural results for a CrS_5O co-ordination sphere have not previously been reported. The average Cr–S bond length, 2·406 Å, agrees very well with values obtained for the tris-chelated dithiocarbamate complexes $[Cr(S_2CNC_4H_8)_3]$, 2·404;[7] and $[Cr(S_2CNC_4H_8O)_3]$, 2·406 Å.[8]

All three ligands are substantially planar out to the α-carbon atoms of the ethyl groups, with the dithiocarbamate ligands having their normal geometry. The S–O bond length in the oxidized ligand, 1·26(2) Å, is unexpectedly short; this apparent effect may result from the high degree of thermal motion of these two particular atoms.

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† Satisfactory elemental analyses were obtained for both the methyl and ethyl derivatives.

‡ I.r. data reported are on unsolvated species.

§ 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.

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