The Formation of a Novel Quinquedentate N_4O Ligand by Dioxygen Oxidation of *trans*-(*RSSR*)-$[CoCl_2(tet\mathit{a})]ClO_4$†

Donald A. House,*[a] Michelle Harnett,[a] Ward T. Robinson,[a] and M. Claire Couldwell[b]

[a] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*

[b] *Department of Computer Science, Massey University, Palmerston North, New Zealand*

The reaction of O_2 with *trans*-(*RSSR*)-[$CoCl_2$(tet*a*)]ClO_4 in refluxing MeOH containing base (triethylamine) results in the oxidation of one of the *gem*-dimethyl substituents to form a quinquedentate N_4O ligand with a co-ordinated $-CH_2OH$ group.

Several isomeric forms of *trans*-[$CoCl_2$(tet*a*)]$^+$ (Figure 1) have now been isolated from the O_2 oxidation of $CoCl_2 \cdot 6H_2O$ and tet*a* in methanol at room temperature.[1] The most abundant of these is the water-insoluble *trans*-[$CoCl_2$(tet*a*)]ClO_4 isomer reported by Whimp and Curtis.[2] The configuration of the secondary NH groups in this form has been assigned as *RSSR*.[3]

When the oxidation is performed at reflux temperature, a considerable quantity of dark green crystals can be isolated after treatment of the oxidised mixture with HCl–$HClO_4$.

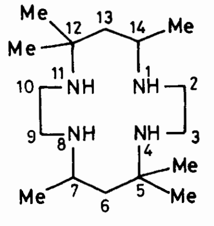

Figure 1. tet*a* (7*R*, 14*S*).

This material gave satisfactory analytical data for [$CoCl(OH_2)$(tet*a*)]$(ClO_4)_2$, but we were surprised that a product of this composition could be recovered unchanged by recrystallisation from concentrated HCl. Addition of $ZnCl_2$ to an HCl solution of the perchlorate salt produced crystals of the $ZnCl_4{}^{2-}$ (monohydrate) salt, suitable for single-crystal *X*-ray analysis.‡ The same product can also be isolated (after HCl–$ZnCl_2$ work-up) by direct O_2 oxidation of *trans*-(*RSSR*)-[$CoCl_2$(tet*a*)]ClO_4 in refluxing MeOH containing triethylamine.

Solution of the *X*-ray crystal structure proceeded without difficulty, and showed that one of the *gem*-dimethyl groups

---

† tet*a* = C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane.

‡ *Crystal Data:* $C_{16}H_{38}Cl_5CoO_2N_4Zn$, $M = 620.09$, monoclinic, space group $P2_1/c$, $a = 17.318(3)$, $b = 9.535(4)$, $c = 16.855(4)$ Å, $\beta = 112.03(2)°$, $U = 2580.0$ Å^3, $Z = 4$, $F(000) = 1280$, μ(Mo-K_α) = 21.4 cm^{-1}. The structure was solved by conventional heavy-atom methods and refined to $R = 0.037$ for 2539 observed reflections ($2\theta < 53°$ at ambient temperature) on a Nicolet R3m diffractometer using monochromatised Mo-K_α *X*-radiation. Atomic co-ordinates 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.

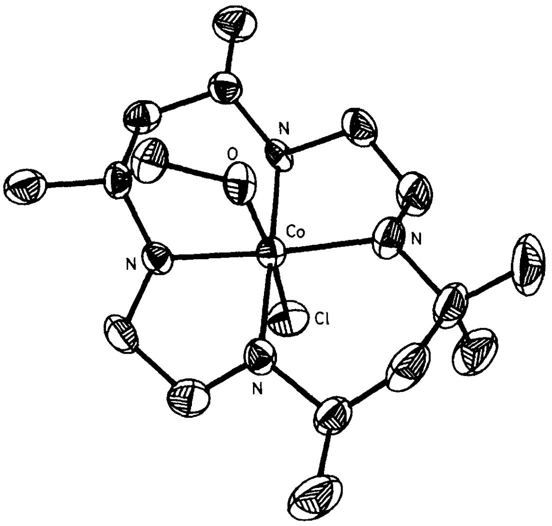

Figure 2. The structure of the complex obtained by the oxidation of $[CoCl_2(teta)]ClO_4$.

had been oxidised to a $-CH_2OH$ group, with the oxygen atom co-ordinated in the axial position (Figure 2). This formulation as a quinquedentate N_4O ligand accounts for the unusual chemistry, and differs by only 2 H atoms from that of the presumed chloro-aqua cation.

The i.r. (KBr disk), ^1H n.m.r. [anhydrous $(CD_3)_2SO$], and ^{13}C n.m.r. spectra (0.1 M HCl) of the perchlorate salt are fully consistent with an OH group co-ordinated to cobalt(III), despite the fact that the proton was not located in the structure analysis.

The facile conversion of an unactivated $-CH_3$ to a $-CH_2OH$ unit is quite remarkable. Dioxygen is a necessary component of the reaction, as when it is replaced by dinitrogen the starting *trans-RSSR*-dichloro-complex is recovered.

We thank the New Zealand University Grants Committee for financial support.

Received, 26th March 1984; Com. 405

References

1 M. Harnett and D. A. House, unpublished research.
2 P. O. Whimp and N. F. Curtis, *J. Chem. Soc., A*, 1966, 867.
3 D. A. House and Othman Nor, *Inorg. Chim. Acta*, 1983, **72**, 195.