The Structure of *trans*-Chloronitrosylbis(ethylenediamine)cobalt(III) Perchlorate: Structural *trans* Effect of the NO⁻ Ligand

By D. A. SNYDER and D. L. WEAVER*

(*Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania* 15213)

Summary The NO^- group in the $[CoCl(NO)(en)_2]^+$ ion exhibits a strong structural *trans* influence.

IN most nitrosyl complexes of transition metals the NO group acts as a σ-donor. However, it has recently become apparent that NO can also function as a Lewis acid. Some examples of the latter behaviour include the oxidative addition[1] of NO^+ to $[IrX(CO)(PPh_3)_2]$; X = Cl or I, to form the $[IrX(CO)(NO)(PPh_3)_2]^+$ ion and several complexes[2] of the formulation $[MX(NO)L_2]^+$; M = Cr, Fe, Co; L = ethylenediamine(en), *o*-phenylenebis(dimethylarsine). The structure of one of these complexes, $[CoCl(NO)(en)_2][ClO_4]$, has been determined by us to elucidate the mode of co-ordination of the NO group.

trans-Chloronitrosylbis(ethylenediamine)cobalt(III) perchlorate, $CoC_4H_{16}N_5O_5Cl_2$, crystallizes as red-brown parallelepipedons in the monoclinic space group $P2_1/c$ with $a = 6{\cdot}636(1)$, $b = 16{\cdot}003(2)$, $c = 12{\cdot}315(2)$ Å, $\beta = 103{\cdot}74$ (2)°, $Z = 4$, $D_m = 1{\cdot}80$, $D_c = 1{\cdot}798$. Complete three-dimensional intensity data (2θ Mo-$K_\alpha < 45°$) were collected on a G.E. XRD-5 automatic diffractometer. A total of 1783 independent reflections were measured of which 1178 were judged to be above background. The structure was solved by the standard heavy-atom technique and refined to a conventional R factor of 6·4%.

The cobalt atom has the expected octahedral co-ordination in the $[CoCl(NO)(en)_2]^+$ cation and the two ethylenediamine rings assume a gauche configuration (see Figure). The average Co–N(en) distance of 1·964(5) Å is comparable to other Co^{III}–N single bond distances,[3] but the Co–N(NO) distance of 1·813(12) Å is significantly shorter and indicates that there is some multiple character in this bond.

A Co–N–O angle of 121·3(1·2)° and an N–O distance of 1·14(2) Å are found. A suitable formalism for describing the bonding of the NO group in this complex is one in which the $N{=}O^-$ moiety, which contains an sp^2 hybridized

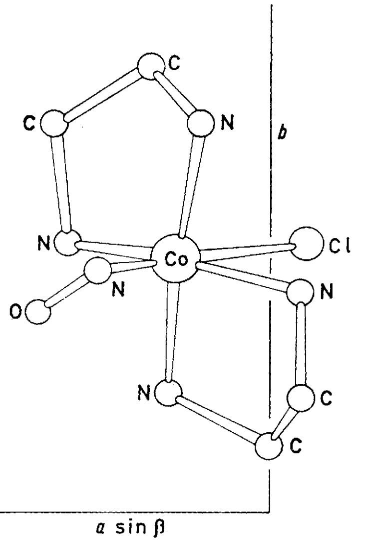

FIGURE. *The structure of the* $[CoCl(NO)(en)_2]^+$ *cation viewed down the crystallographic* c *axis.*

nitrogen atom, is σ-bonded to Co^{III} with some concomitant π-bonding interaction occurring between the cobalt and nitrogen atoms.

The NO^- group exhibits a strong structural *trans* influence as evidenced by the remarkably long Co–Cl distance of 2·576(3) Å. This is to our knowledge the largest structural *trans* effect (*ca.* 0·30 Å) yet determined for an octahedral d^6 complex.[4] There is evidence for a *trans* effect of a similar magnitude[5] in $[Co(NH_3)_5NO]Cl_2$ although crystals of this compound are twinned.†

All of the hydrogen atoms in this structure were located and show that hydrogen bonding occurs between the ClO_4^- group oxygen atoms and the amine hydrogen atoms. There is also some evidence from a difference Fourier map of a small partial disorder of the oxygen atom of the NO group.

(*Received, October 2nd,* 1969; *Com.* 1492.)

† *Added in proof.* Since this communication was submitted a report has appeared in which the NO^- group in $Rh(NO)(PPh_3)_3$ labilizes a *trans*-phosphine ligand and oxidative addition of X–Y to this complex proceeds with loss of phosphine: $Rh(NO)(PPh_3)_3 + X\text{–}Y \rightarrow Rh(NO)(X)(Y)(PPh_3)_2 + PPh_3$. (X–Y = I_2 or PhCOCl). J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 1969, **91**, 5659.

[1] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1969, **6**, 1282.
[2] R. D. Feltham, W. Silverhorn, and G. McPherson, *Inorg. Chem.*, 1969, **6**, 344, and references therein.
[3] N. E. Kime and J. A. Ibers, *Acta Cryst.*, 1969, B**25**, 168.
[4] See, for example, A. C. Skapsi and P. G. H. Troughton, *Chem. Comm.*, 1969, 666.
[5] D. Hall and A. A. Taggart, *J. Chem. Soc.*, 1965, 1359; D. Dale and D. C. Hodgkin, *ibid.*, p. 1364.