Isolation and Characterization of Chloro(ethyl)dimethylglyoximatodimethylglyoximecobalt(III) Hydrate. A Protonated Cobaloxime

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Summary A monoprotonated cobaloxime, [EtCo(dmg)(dmgH)Cl]H_2O, has been isolated and characterized by i.r., u.v., and *X*-ray methods which indicate a dimethylglyoxime oxygen as the site of protonation.

Protonated dimethylglyoxime complexes of the type Co(dmg)(dmgH)Cl_2† have been isolated and characterized by i.r. spectroscopy.[1] Recent studies[2,3] which postulate the existence in solution of protonated alkyl-cobalt(III) complexes containing dimethylglyoxime as a ligand prompt us to report here the isolation of the first well characterized crystalline alkylcobaloxime complex in protonated form, [EtCo(dmg)(dmgH)Cl]H_2O.‡

The neutral complex [EtCo$(dmg)_2OH_2$][4] was protonated by dissolving it in 6N-HCl, adding methanol, warming to 60 °C, and then cooling to 0 °C when deep orange hexagonal plates were isolated.§ Ready dissociation in water according to equation (1) is shown by pH measurements, positive

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† (dmg) = dimethylglyoxime monoanion [MeC:(NOH)C:(NO)Me]$^-$.

‡ Espenson[2] reported briefly the isolation of a compound with approximate composition HMeCo$(dmg)_2$SCN, but gave no analytical or physical data.

§ Satisfactory analytical data were obtained for all compounds reported here.

$$[EtCo(dmg)(dmgH)Cl] \overset{H_2O}{\rightleftharpoons} [EtCo(dmg)_2OH_2]+Cl^-+H_3O^+ \quad (1)$$

Cl^- test, and electronic spectra. The i.r. and electronic (mull and solution) spectra, which will be discussed elsewhere, both suggest a dimethylglyoxime oxygen as the site of protonation. This was confirmed by a single-crystal X-ray analysis.

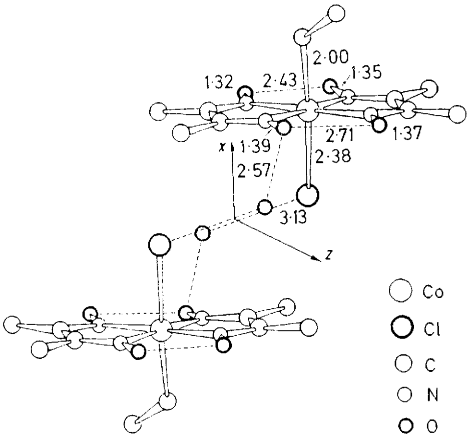

FIGURE. *Some important distances* (Å) *in* [EtCo(dmg)(dmgH)-Cl]H_2O; *e.s.d.'s are* $+0{\cdot}014$ Å *for* N–O, O–O, *and* Co–C *and* $\pm 0{\cdot}004$ Å *for* Co–Cl. *Hydrogen bonds are denoted by broken lines.*

Crystals of [EtCo(dmg)(dmgH)Cl]H_2O are monoclinic, space group $C2/c$ (C_{2h}^6), $a = 31{\cdot}89$, $b = 7{\cdot}61$, $c = 14{\cdot}49$ Å, $\beta = 116{\cdot}95°$, $Z = 8$. The crystal structure was solved by the heavy-atom method and refined by full-matrix least-squares to $R = 0{\cdot}123$ for 1593 independent X-ray reflections from photographic data. The crystals contain centrosymmetrically related pairs of complex molecules bridged by a hydrogen-bonded water of solvation as shown in the Figure. The cobalt atom lies in the plane defined by the approximately equidistant nitrogen atoms, mean Co–N = 1·90 Å. None of the C–C or C–N distances deviates significantly from the mean [C(sp^3)–C(sp^2) = 1·48, C(sp^2)–C(sp^2) = 1·47, C(sp^2)–N = 1·29 Å]. The Co–C distance, 2·00(±0·015) Å, is close to that of 1·990(7) Å in *NN'*-ethylenebis(salicylideneiminato)ethylcobalt(III),[5] 2·04 Å in *O*-methyl-(Co–C)-carboxymethyl(bisdimethylglyoximato)-pyridinatocobalt(III)[6] and 1·97 Å in cyanocobalamin.[7]

Noteworthy is the highly significant difference between the two dimethylglyoxime O–H · · · O separations ($\Delta/\sigma = 18$). We ascribe this to the protonation of one oxygen atom which then may participate in an intermolecular hydrogen bond to the water molecule of solvation with concomitant weakening of the intramolecular bond. The shorter O–H · · · O distance (2·43 Å) is close to those observed in similar systems, *e.g.* *O*-methyl-(Co–C)-carboxymethyl(bisdimethylglyoximato)pyridinatocobalt(III) (2·49, 2·51 Å),[6] bis(dimethylglyoximato)nickel(II) (2·44 Å),[8] bis(ethylmethylglyoximato)nickel(II) (2·45 Å),[9] and bis(glyoximato)nickel(II) (2·45 Å),[10] where intramolecular hydrogen bonding occurs.

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