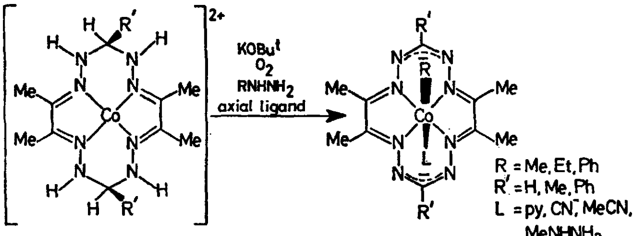
Organo-cobalt(III) Complexes with a Thermally Accessible Paramagnetic State

By VIRGIL L. GOEDKEN* and SHIE-MING PENG
(*Department of Chemistry, University of Chicago, Chicago, Illinois* 60637)

Summary New Co^{III}-alkyl complexes of the type $[Co(C_{10}H_{14}N_8)(L)(R)]$ have anomalous n.m.r. spectra which have been ascribed to paramagnetic contact shifts arising from a thermally populated triplet state.

RECENT studies have shown that all known Co^{III}-alkyl complexes are diamagnetic.[1] The ^1H n.m.r. spectra of methyl-cobalt(III) complexes are generally observed in the range 2·5 to 0 p.p.m.,[2] with the exception of porphyrins[3] and phthalocyanines[4] which are observed at −5·15 and −6·1 p.p.m. due to the diamagnetic shielding of the equatorial ring currents. We now report the synthesis and characterisation of a number of six co-ordinate Co^{III}-alkyl complexes which, although virtually diamagnetic,[5] exhibit anomalous n.m.r. behaviour which we attribute to paramagnetic contact shifts arising from a thermally populated triplet state. The magnitude of the observed n.m.r. shifts is small when compared with the contact shifts associated with complexes having paramagnetic ground states. The population of the thermally accessible paramagnetic state in these complexes is too small to be determined from conventional bulk susceptibility measurements because the contributions from temperature independent paramagnetism and ligand diamagnetism cannot be obtained independently, nor are they negligible.



R = Me, Et, Ph
R' = H, Me, Ph
L = py, CN^-, MeCN, $MeNHNH_2$

(I) (II)

Treatment of the Co^{II} bis-α-di-imine complex, (I), with organic hydrazines, oxygen, and alkoxide anions results in a complex series of reactions yielding molecular organo-Co^{III} complexes of the type, $[Co(C_{10}H_{14}N_8)(L)(R)]$, (II). The net result of these reactions is; (1) the introduction of two additional double bonds into the six-membered chelate rings together with the loss of a proton from each ring yielding three-atom delocalized six-membered rings and (2) oxidative deamination of the organic hydrazine and the formation of organo-Co^{III} bonds.[6]

The most striking feature associated with the alkylcobalt(III) complexes (II) is their anomalous n.m.r. spectra. In general the spectra are characterised by large downfield shifts for axial ligands and upfield shifts for those protons located in the equatorial plane of the macrocyclic ligand. For example, the ^1H n.m.r. resonances for $[Co(C_{10}H_{14}N_8)(py)(Me)]$ [$\delta([^2H_5]$-py) 9·00 (Co–Me), 8·7, 13·9 (py), 4·22 (C–H), and 0·57 (ligand Me's)] are all outside the ranges expected. The ^1H n.m.r. spectra of the complexes are markedly dependent on changes in the axial ligand, minor changes in the macrocyclic ligand, solvent, and temperature. Changing one nitrogen donor for another led to only minor changes in the spectra. However, exchanging pyridine for a π-acceptor such as cyanide lowers the Co–Me absorption from 8·04 to 6·93 p.p.m. ($[^2H_5]$-py,D_2O). Substituting methyl groups for the hydrogen atoms of C(1) and C(4), (Figure), a position relatively isolated from the co-ordination sphere, shifts the absorption of the Co^{III}-Me group from 8·04 to 6·56 p.p.m. in $CDCl_3$.

The strongest evidence supporting our contention that the anomalous n.m.r. spectra are due to paramagnetic contact shifts arising from a thermally populated paramagnetic state is derived from the temperature dependence of the n.m.r. spectra. Cooling a sample of $[Co(C_{10}H_{14}N_8)(MeNHNH_2)(Me)]$ from +50 °C to −50 °C in $CDCl_3$ results in a shift of the absorption maxima of Co^{III}–Me from 8·16 to 7·59 p.p.m., the direction expected for an increase in the population of a singlet ground state. The n.m.r. spectra of the complexes are independent of concentration and are reproducible thus eliminating the possibility of contact shifts resulting from rapid electron exchange between the cobalt(III)-alkyl complexes and some paramagnetic impurity. Both solutions and solid samples give weak, isotropic e.s.r. signals ($g = 2{\cdot}01$) at room temperature which disappear on cooling the sample to liquid N_2 temperature.

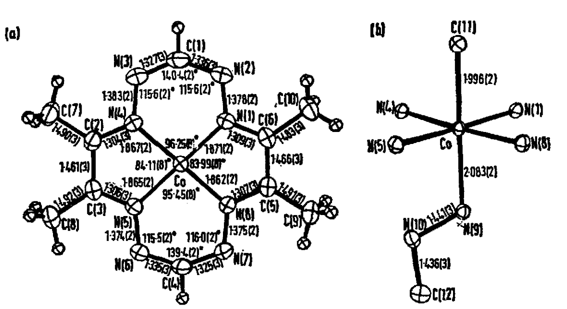


FIGURE. Interatomic distances and angles in $[Co(C_{10}H_{14}N_8)(Me)(NH_2NHMe)]$ as observed (a) down the axial ligands and (b) from a simplified side view.

The macrocyclic ligands in these complexes contain 16 π-electrons and the possibility that the anomalous ^1H n.m.r. spectra are due to anti-aromatic ring currents similar to those observed for the dianion of 15,16-dimethyldihydropyrene[7] has been considered. The sensitivity of the spectra to solvent, temperature, and ligand substituents is not compatible with this explanation. Furthermore, organo-Co^{III} complexes of a geometrical isomer of this 16π-electron system display normal n.m.r. behaviour.[6]

The crystal structure of the complex, $[Co(C_{10}H_{14}N_8)(NH_2NHMe)(Me)]$, was determined unambiguously to define the double bond arrangement, the extent of delocalization in the macrocyclic ligand, and to shed some light on the magnetic peculiarities of these organo-Co^{III} complexes. The macrocyclic ligand is flat and contains an α-di-imine function in each of the five-membered chelate rings, and a three atom, N–C–N, delocalized system in each of the six-membered chelate rings (Figure). The angles defined by N(2)–C(1)–N(3) and N(6)–C(4)–N(7), 140·2(2)° and 139·4(2)° respectively are unusually wide. This is apparently due to the preference of the N–N–C linkage for an angle less than 120°. Crystal structures of two other compounds having this linkage were found to have angles of 108° and 111°.[8]

The parameters of the inner co-ordination sphere are totally consistent with those reported for a number of organo-Co^{III} complexes[2] with one exception. The average Co-N (planar) distance, 1·866 Å, is shorter, although only slightly, than in other organo-Co^{III} complexes. The crystal structures of three cobaloxime complexes, which are the mostly closely related to our organo-cobalt complexes, have mean Co–N (planar) distances which vary between 1·88 Å and 1·90 Å.[9]

We thank the National Institutes of Health for support.

(*Received*, *25th November* 1974; *Com.* 1428.)

---

[1] Nearly all cobalt(III) complexes are diamagnetic. For some exceptions see M. Gerloch, B. Higson, and E. D. McKenzie, *Chem. Comm.*, 1971, 1149; R. Williams, E. Billing, J. Waters, and H. Gray, *J. Amer. Chem. Soc.*, 1966, **88**, 43; K. A. Jensen, P. H. Nielsen, and C. Pederse, *Acta Chem. Scand.*, 1963, **17**, 1115.

[2] D. Dodd and M. D. Johnson, *Organometallic Chem. Rev.*, 1973, **52**, 34.

[3] D. A. Clark, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc.*, (*C*), 1968, 881.

[4] P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc.*, *A*, 1968, 90.

[5] The complexes are diamagnetic, but, when one corrects for the diamagnetic contributions of the ligand, the resulting magnetic moments are in the range of 0·4 to 0·6 B.M. This is also observed for other 'diamagnetic' cobalt(III) complexes and is due to the second order Zeeman effects, see C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, 1957, **11**, 479; J. W. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 1957, **53**, 601.

[6] V. L. Goedken, S.-M. Peng, and Y. Park, *J. Amer. Chem. Soc.*, 1974, **96**, 284.

[7] R. H. Mitchell, C. E. Klopfenstein, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1969, **91**, 4931.

[8] R. Mason, K. M. Thomas, A. R. Galbraith, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1973, 297; V. L. Goedken and S.-M. Peng, *J. Amer. Chem. Soc.*, 1974, **95**, 5774.

[9] P. G. Lenhert, *Chem. Comm.*, 1967 980; D. McFadden and A. T. McPhail *J.C.S. Dalton*, 1974, **363**; A. L. Crumbliss, J. T. Bowman, P. Gauss, and A. T. McPahil, *J.C.S. Chem. Comm.*, 1973, 415.