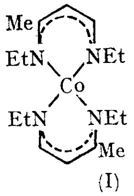
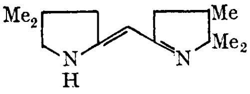
Bis-(*NN'*-diethylbutane-2,4-di-iminato)cobalt(II), a Tetrahedral Cobalt Derivative of a New Nitrogen Chelate Group

By R. BONNETT, D. C. BRADLEY,* and K. J. FISHER
(*Department of Chemistry, Queen Mary College, Mile End Road, London, E.*1.)

PREVIOUS attempts to prepare bisdiethylamidocobalt(II) from reactions involving lithium diethylamide and cobalt(II) chloride were unsuccessful but a small yield of a volatile (120°/0·1 mm) brown liquid, $C_{16}H_{32}N_4Co$, was obtained.[1] We now formulate this compound as (I), bis-(*NN'*-diethylbutane-2,4-di-iminato)cobalt(II), a member of the little-known series of nitrogen analogues of metal β-diketonates. The molecular formula was established by precision mass spectrometry (M^+, 337·1819. Calc. for $C_{16}H_{30}N_4{}^{59}Co$, 337·18015). The occurrence of the base peak at *m/e* 199, corresponding to the loss of one ligand (less one proton), supports a structure with two bidentate ligands rather than a structure with a quadridentate group.



(I)



(II)

Further support for structure (I) came from the electronic spectrum which closely resembled in general form that of the cobalt(II) derivative[2] of the vinylogous amidine (II). In the i.r. region bands were observed at 3145 and 3072 (m, quasi-aromatic C–H stretching), 1569 (vs, $N\cdots C\cdots C\cdots C\cdots N$), and 725 cm.$^{-1}$ (s, out-of-plane C–H deformation), again in agreement with (I). No evidence was found for the presence of C–H bonds.

The u.v. spectrum gave an intense solvent-sensitive band at *ca.* 29,000 cm.$^{-1}$ (ϵ 27,900) with a shoulder at 34,500 cm.$^{-1}$ (ϵ 16,700). In the visible and near i.r. spectrum weak *d–d* bands due to tetrahedrally co-ordinated cobalt(II) appeared, thus: $\nu_1[{}^4T_2(F) \leftarrow {}^4A_2]$, 5900; $\nu_2[{}^4T_1(F) \leftarrow {}^4A_2]$, 9800; $\nu_3[{}^4T_1(P) \leftarrow {}^4A_2]$, 22,050 cm^{-1}. The spectrum is of special interest in showing the ν_1 band which is not usually observed in tetrahedral Co^{II} spectra. From these assignments were calculated 10*Dq*, 5900 cm.$^{-1}$ and the Racah parameter B', 944 cm.$^{-1}$ (*cf.* free ion B, 972 cm.$^{-1}$). The corrected molar susceptibilities (T = 113—298°K) gave a Curie–Weiss plot ($\theta = -2°$) and an effective magnetic moment of 4·13 B.M. which, with the above value of 10*Dq*, gave the apparent spin-orbit coupling constant λ', 96 cm.$^{-1}$ (*cf.* free ion λ_0, 178 cm.$^{-1}$) and the electron delocalization factor k, 0·75. Therefore the new ligand produces a high ligand field and this causes a low paramagnetic moment. Indeed, the n.m.r. spectrum of the complex (I) has been observed, which shows large contact shifts[3] and is spread over the range τ −172 to 127. It is probable that the tetrahedral configuration of (I) results from the steric interaction of the *N*-ethyl groups which destabilize a planar system. The work of Everett and Holm[4] on bis-(β-keto-amino)cobalt(II) compounds shows that the square planar–tetrahedral equilibrium is sensitive to steric factors.

In contrast to dialkylamido–metal compounds the complex (I) is not readily hydrolysed by water or by dilute alkali but it is sensitive to acids, which release the cobalt ion and give the salt of the ligand base. The base itself, $C_8H_{16}N_2$, (III), was isolated from a reaction of the complex (I) with benzimidazole, but it was very unstable and it has not been possible to analyse it. Solutions of the base (III) as its acid salts showed intense absorption at 32,500 cm.$^{-1}$ [*cf.* ref. 2, (II): (EtOH) ν_{max} 31,250 (ϵ 43,500) (EtOH–HCl) ν_{max} 31,250 cm.$^{-1}$ (ϵ 44,000)]. The ligand anion $C_8H_{15}N^-$ is considered to be derived by the dehydrogenation and coupling of two diethylamide ions: possible mechanisms for this, together with full details of the chemical and spectroscopic properties of complex (I), will be reported.

One of us (K. J. F.) thanks Queen Mary College for the award of a College Postgraduate Studentship, and Dr. D. Shaw for the n.m.r. spectrum of (I).

(*Received, May 20th,* 1968; *Com.* 631.)

---

[1] D. C. Bradley, K. Chivers, H. Cross, I. M. Thomas, and E. G. Torrible, reported in U.S. Air Force Technical Reports, May 1961, October 1962, August 1964.

[2] R. F. C. Brown, V. M. Clark, I. O. Sutherland, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2109.

[3] *cf.* G. N. LaMar, *Inorg. Chem.*, 1967, **6**, 1939.

[4] G. W. Everett, jun., and R. H. Holm, *J. Amer. Chem. Soc.*, 1966, **88**, 2442.