# Letters

## Cobalt(II)–ether bonds

NEWKOME *et al.*[1] recently stated that ' ether complexes of the later transition elements are not expected to be particularly stable, especially in the +2 oxidation state ' and that the $Co^{II}$–O(ether) bond in a particular species [(8) of ref. 1] was ' novel '. These words could lead to misapprehensions that should be corrected.

An etherate of $CoBr_2$ has been known for many years.[2] Solids $[MCl_2(diox)]$, $[MBr_2(diox)]$, and $[MBr_2(diox)_2]$ (M = Co or Ni, diox = 1,4-dioxan) have been shown from magnetic data to contain octahedral $M^{II}$ with dioxan oxygen as ligand.[3] Crystal structures have been reported in which five-co-ordinate [4] or six-co-ordinate [5,6] $Co^{II}$ is attached to ether oxygen in a macrocyclic [5] or chelating [4,6] ligand. We have dissolved anhydrous cobalt bromide, and $CoBr_2 \cdot 1.5$thf, in carefully dried tetrahydrofuran (thf), to give indistinguishable solutions containing $[CoX_4]^{2-}$ (X = Br) anions (and hence, perforce, ether-solvated $Co^{2+}$ cations) (similar behaviour had been reported [7] for $CoCl_2$ and $CoBr_2$ methanol and acetone solutions), while solutions of $CoCl_2$ in benzene containing dicyclohexano-18-crown-6 clearly show both octahedral and tetrahedral $Co^{II}$.

Thus complexes with $Co^{II}$–ether oxygen bonds are neither unusual, nor inaccessible.

PAUL S. BRATERMAN *
ALISON E. LESLIE
BRIAN S. WALKER

*Department of Chemistry*
*University of Glasgow*
*Glasgow G12 8QQ*

[0/710 *Received*, 13*th May*, 1980]

[1] G. R. Newkome, D. K. Kohli, and F. Fronczek, *J.C.S. Chem. Comm.*, 1980, 9.
[2] F. Ducelliez and A. Raynaud, *Bull. Soc. chim. France*, 1914, **15**, 599.
[3] G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Chem. Soc.* (*A*), 1968, 1842.
[4] P. Dapporto, G. Fallani, and L. Sacconi, *J. Co-ordination Chem.*, 1971, **1**, 269.
[5] L. G. Armstrong, L. F. Lindoy, M. McPartlin, G. M. Mocker, and P. A. Tasker, *Inorg. Chem.*, 1977, **16**, 1665.
[6] J. Estienne and R. Weiss, *J.C.S. Chem. Comm.*, 1972, 862.
[7] W. C. Nieuwfoort, G. A. Wesselink, and E. H. A. M. Van Der Wee, *Rec. Trav. chim.*, 1966, **85**, 397.

NEWKOME *et al.* reply. In support of our original [1] statements with regard to the observation of such bonds in the crystal of a macrocomplex, we are compelled to point out the dearth of examples [2] of these relatively long weak $Co^{II}$–O(ether) bonds *in the solid state*. Our initial remarks dealt exclusively with the established crystal structural data and did not pertain to the solvation of $Co^{II}$ by ethers.[3] Braterman *et al.* have based their challenge on an ill conceived fusion of information from crystal studies with that from solution studies. The considerations of solution data to which they refer are irrelevant to discussion of the rarity of $Co^{II}$–O(ether) bonds in the solid state. However, their list of references does buttress our argument that the $Co^{II}$–O(ether) bond is unusual in crystalline complexes, although not unexpected.

G. R. NEWKOME
D. K. KOHLI
F. FRONCZEK

*Department of Chemistry*
*Louisiana State University*
*Baton Rouge*
*Louisiana* 70803
*U.S.A.*

[1] G. R. Newkome, D. K. Kohli, and F. Fronczek, *J.C.S. Chem. Comm.*, 1980, 9.
[2] P. Dapporto, G. Fallani, and L. Sacconi, *J. Co-ordination Chem.*, 1971, **1**, 269; J. Estienne and R. Weiss, *J.C.S. Chem. Comm.*, 1972, 862; F. Mathieu and R. Weiss, *ibid.*, 1973, 862; L. G. Armstrong, L. F. Lindoy, M. McPartlin, G. M. Mocker, and P. A. Tasker, *Inorg. Chem.*, 1977, **16**, 1665; E. M. Holt, R. A. Palmer, and T. B. Vance, jun., Abstracts, Winter Meeting of the American Crystallographic Association, 1980, **24**.
[3] G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3119.