Electrochemical Indications of New Oxidation States in Transition-metal Dicarbollide Complexes

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Summary Polarographic and cyclic voltammetric evidence is given for previously unreported low oxidation states of some transition-metal dicarbollide complexes.

TRANSITION-METAL complexes of polyhedral carborane ligands have received considerable attention recently.[1] In many cases the complexes have been shown to support reversible one-electron transfers between adjacent formal metal oxidation states. We have performed electrochemical experiments using judiciously purified solvents and have obtained evidence for low oxidation states of transition metals in π-dicarbollide complexes which were not revealed in earlier studies of this type.[1c,1d] The newly observed species possess varying stabilities in acetonitrile, but are more stable in 1,2-dimethoxyethane. This is the first evidence that the π-bonded dicarbollide ligand can stabilize metals in low, as well as high,[1b] oxidation states.

Polarographic data for the π-(3)*-dicarbollyl complexes of nickel and cobalt*

Compound	Solvent[a]	$E_{1/2}$[b]	I_d[c]
$[\pi\text{-(3)-1,2-}B_9C_2H_{11}]_2Ni$	MeCN	+0·25[d]	3·56
		−0·57[d]	6·94
		−2·10	11·30
	DME	+0·28	2·54
		−0·62	5·00
		−2·21	7·88
$[Et_4N][(\pi\text{-(3)-1,7-}B_9C_2H_{11})_2Ni]$	MeCN	−0·92[d]	3·34
		−2·09	8·16
	DME	−0·94	2·79
		−2·25	5·06
$(\pi\text{-}C_5H_5)Co(\pi\text{-(3)-1,2-}B_9C_2H_{11})$	MeCN	−1·21[d]	4·43
		−2·11	13·6
	DME	−1·19	4·65
		−2·21	9·10
$[Et_4N][(\pi\text{-(3)-1,2-}B_9C_2H_{11})_2Co]$	MeCN	−1·36[d]	3·47
		−2·24	6·72
	DME	−1·37	2·14
		−2·37	4·15
$[Et_4N][(\pi\text{-(3)-1,7-}B_9C_2H_{11})_2Co]$	MeCN	−1·14[d]	3·50
		−2·52	7·85
	DME	−1·21	2·51
		−2·70	5·09
$[Me_4N]_2[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})]$	MeCN	−1·48[d]	3·75
		−2·36	8·75
	DME	−1·49	2·18
		−2·43	4·31

[a] MeCN = acetonitrile, 0·10 M in tetrabutylammonium hexafluorophosphate (TBAHFP); DME = dimethoxyethane, 0·15 M *in* TBAHFP.

[b] Volts *versus* the saturated calomel electrode.

[c] $I_d = i_d/Cm^{2/3}t^{1/6}$, where i_d = total diffusion current at end of drop life, C = concentration of electroactive species (*ca.* 1 mM), m = flow rate, t = drop time of capillary.

[d] Previously reported in refs. 1c and 1d.

Several [π-(3)-dicarbollyl] complexes of nickel and cobalt were studied by polarography and cyclic voltammetry at a mercury electrode in acetonitrile and 1,2-dimethoxyethane solutions containing tetrabutylammonium hexafluoro-phosphate as supporting electrolyte. Each of the complexes studied exhibits a previously unreported reduction wave at a rather highly negative potential. The results are collected in the Table where, for the sake of comparison, data on all the reduction waves have been included. The new polarographic waves in dimethoxyethane are established as reversible, diffusion-controlled, one-electron processes from the values of the limiting current constants (I_d in the Table) and plots of log $[i_d - i)/i]$ against E, which gives slopes close to the theoretical value of −59 mv expected for this type of electrode process. Cyclic voltammetry experiments at sweep rates of about 1·8 v/s in dimethoxyethane show an anodic peak current coupled to the last reduction peak, with an iR compensated[2] peak-to-peak separation of approximately 60 mv, which is characteristic of diffusion-controlled one-electron charge transfer. Corresponding ratios of anodic peak current to the cathodic peak current i_{pa}/i_{pc} were 1·0, again indicating the reversibility of the electrochemical reactions. With the exception of the so-called "double-barrelled" cobalt complex,[1c] the new species possess cobalt and nickel atoms in the *formal* + 1 oxidation state.

Only the bis-$[\pi\text{-(3)-1,2-}B_9C_2H_{11}]_2Co$ complex gives an uncomplicated reversible reduction to the formal Co^I species (as the trianion) in acetonitrile. The remainder of the compounds give I_d values corresponding to the uptake of a non-integral number of electrons per molecule for the new wave. These apparent n-values ($n > 1$) are obtained by using as an internal standard for a diffusion-controlled one-electron process the I_d value of the first reduction step. They may be calculated from the data in the Table. Such observations suggest an ECE-type mechanism.[3] This hypothesis is supported further by cyclic voltammetry experiments. In acetonitrile cyclic voltammograms of the latter cobalt compounds exhibit ratios of i_{pa}/i_{pc} which are dependent on the scan rate, in a manner consistent with a reaction mechanism involving a follow-up chemical reaction coupled to an initial one-electron transfer step.[3,4]

The electrode processes involving the nickel(I) species in acetonitrile appear to be somewhat different than those found in the cobalt series. Cyclic voltammetry experiments suggest that the Ni^I species initially formed undergo rapid follow-up reaction or rearrangement to give one or more products oxidizable at a less negative potential.

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[1] (a) M. F. Hawthorne, *Accounts Chem. Res.*, 1968, **1**, 281; (b) L. F. Warren, jun., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1970, **92**, 1157, and references contained therein; (c) J. N. Francis and M. F. Hawthorne, *ibid.*, 1968, **90**, 1663; (d) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, jun., and P. A. Wegner, *ibid.*, p. 879; (e) J. L. Little, P. S. Welcker, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, 1970, **9**, 63; (f) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *ibid.*, 1967, **6**, 1696.

[2] R. S. Nicholson, *Analyt. Chem.*, 1965, **37**, 1351; E. R. Brown, T. G. McCord, D. E. Smith, and D. D. DeFord, *ibid.*, 1966, **38**, 1119.

[3] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1965, **37**, 178.

[4] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.