The Reduction of Thioether and Carboxylate Chelates of Cobalt(III) by Chromium(II)

By MICHAEL GILROY and FRANK A. SEDOR
(*Department of Chemistry, University of Florida, Gainesville, Florida* 32601)

and LARRY E. BENNETT*
(*Department of Chemistry, San Diego State College, San Diego, California* 92115)

Summary The rates of reduction by chromium(II) of $Co(en)_2(NH_2CH_2CO_2)^{2+}$ (carboxylate-bridged), $Co(en)_2(O_2CCH_2SMe)^{2+}$ (carboxylate-bridged) and $Co(en)_2(NH_2CH_2SMe)^{3+}$ (outer-sphere) indicate reactivity advantages for *chelated* bridging carboxylate and nonbridging *cis* thioether ligands in inner-sphere reactions and a high reactivity associated with thioether functions in outer-sphere reactions.

THE influence of a co-ordinated thioether function on the redox activity of a transition metal complex attracts special interest in view of the co-ordination of methionine sulphur in both oxidized and reduced forms of cytochrome C.[1] We have prepared $Co(en)_2(O_2CCH_2SMe)^{2+}$ and $Co(en)_2(NH_2CH_2CH_2SMe)^{3+}$. Both complexes are reduced in 1:1 molar ratios by chromium(II): $-d[Co^{III}]/dt = k[Co^{III}][Cr^{II}]$, over ten-fold variations in $[Cr^{II}]$ and $[H_3O^+]$ neighbouring 10^{-2} M (1·0 M ionic strength, $LiClO_4$–$HClO_4$, 25 °C).

The reduction of $Co(en)_2(O_2CCH_2SMe)^{2+}$ yields $Cr(H_2O)_5(O_2CCH_2SMe)^{2+}$ [λ_{max} 567(ϵ 26·7), 412(25·9) nm] as the only isolable Cr^{III} product establishing the mechanism as inner-sphere. Failures to detect deviations from pseudo-first order linearity (> 90% reaction) or appreciable spectral change subsequent to the redox reaction under first-order conditions, $2{\cdot}7\ s^{-1} < k\ [Cr^{II}] < 27\ s^{-1}$, are consistent with this being the initial product of a carboxylate-bridged reaction.† Further support for this mechanism can be adduced from the data in the Table. If the reduction were sulphur-bridged the reactivity of $Co(en)_2(NH_2CH_2CH_2SMe)^{3+}$ would almost certainly be higher than observed since a change from carboxylate to amine in the *cis* non-bridging position should diminish the rate even less than in the *trans* position[3] where the factor is 50 (IV and III in Table). Secondly, our studies of the reduction of $Co(en)_2(O_2CCH_2NH_2)^{2+}$, $-d[Co^{III}]dt = k[Co^{III}][Cr^{II}]$, to yield $Cr(H_2O)_5(O_2CCH_2NH_3)^{3+}$ reveal a six-fold rate advantage over the analogous reduction of $Co(NH_3)_5(O_2CMe)^{2+}$. This occurs in spite of a rate decrease expected for a change from ammine to ethylenediamine ligands[3] although the enthalpic barrier does increase slightly. The advantage for the chelated carboxylate ligand resides in a diminished entropic barrier which presumably reflects a greater steric accessibility of the bridging carboxylate.

Reactivity parameters for reduction of cobalt(III) *complexes by chromium*(II)

	Complex	k, $M^{-1}\ s^{-1}$	$\Delta H^‡$, kcal mole^{-1}	$\Delta S^‡$, e.u.	Reference
		Inner-Sphere Reductions			
I	$Co(en)_2(MeSCH_2CO_2)^{2+}$	274	8·5	−19	this work
II	$Co(en)_2(NH_2CH_2CO_2)^{2+}$ ..	2·2	8·8	−27	this work
III	$Co(NH_3)_5(O_2CMe)^{2+}$	0·35	8·2	−33	ref. 6
IV	*trans*-$Co(NH_3)_4(O_2CMe)_2^+$ ..	15			ref. 7
V	*cis*-$Co(NH_3)_4(H_2O)(O_2CMe)^{2+}$ ..	47			ref. 7
		Outer-Sphere Reductions			
VI	$Co(en)_2(MeSCH_2CH_2NH_2)^{3+}$ ..	0·38	5·4	−42	this work
VII	$Co(en)_3^{3+}$	*ca.* 2×10^{-5}			ref. 8
VIII	$Co(NH_3)_6^{3+}$	$8{\cdot}9 \times 10^{-5}$			ref. 9
IX	$Co(NH_3)_5py^{3+}$	0·0043	9·8	−36	ref. 10

Thus, the unusually high rate for chromium(II) reduction of $Co(en)_2(O_2CCH_2SMe)^{2+}$, with a six-fold enhancement over that of *cis*-$Co(NH_3)_4(H_2O)(O_2CMe)_2^+$ (carboxylate-bridged), appears primarily attributable to this chelate effect and to the *cis* non-bridging influence of the thioether function being comparable to that of water and substantially higher (125 fold) than that of an amine function. These conclusions are in good qualitative agreement with the trends for the chloride-bridged iron(II) reductions of *cis*-$Co(en)_2(NH_3)Cl^{2+}$ ($k = 1{\cdot}8 \times 10^{-5}$)[3] *vs.* *cis*-$Co(en)_2(H_2O)Cl^{2+}$ ($k = 4{\cdot}6 \times 10^{-4}$)[3] and *cis*-$Co(en)_2Cl_2^+$ ($k = 0{\cdot}0016$)[3] *vs.* *cis*-$Co(NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2)Cl_2^+$ ($k = 1{\cdot}35$).[4] The last result provided the first indication of the high inner-sphere reactivity provisioned by non-bridging thioether donors but reflects the superimposed influences of both *cis* and *trans* variations.

The reduction of $Co(en)_2(NH_2CH_2CH_2SMe)^{3+}$ yields $Cr(H_2O)_6^{3+}$ as the only product isolable by ion-exchange. The redox reaction was monitored over 3—6 half-lives under first-order conditions where $k[Cr^{II}]$ is *ca.* $4{\cdot}3 \times 10^{-3}\ s^{-1}$ with no evidence of a subsequent hydrolysis reaction. Thus, $Cr(H_2O)_6^{3+}$ appears to be the initial product of an outer-sphere reaction. Accepting this mechanism, the rate advantage for the thioether complex, relative to amine and imine examples, is derived from a diminished enthalpic barrier. This is in accord with the expectation that the stretching of a relatively weak cobalt(III)–thioether bond should make a smaller contribution to the activation barrier. The comparison is especially interesting since the effect of histidine, a potential alternate for methionine as a ligand in cytochrome C, on outer-sphere reactivity is expected to lie between those of amine and imine ligands. However, any suggestion that methionine co-ordination in cytochrome C contributes to a high redox activity must be made with caution since the trends described are dependent

---

† This conclusion differs from the one presented previously,[2] which is now regarded as being premature.

on the electronic structure of the metal centre[6] which differs for the present complex and cytochrome C.

We thank Professors Harry B. Gray and Robert G. Linck for helpful comments and the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

(*Received, 22nd November* 1971; *Com.* 2008.)

---

[1] (a) R. E. Dickerson, T. Takano, D. Eisenberg, O. B. Kallai, L. Sampson, A. Copper, and E. Margoliash, *J. Biol. Chem.*, 1970, **24**, 1511; (b) R. E. Dickerson, T. Takano, and O. B. Kallai, Proc. Cold Spring Harbor Symp. Quant. Biol., 36, in the press.

[2] Frank A. Sedor, Ph.D. Thesis, University of Florida 1971.

[3] P. Benson and A. Haim, *J. Amer. Chem. Soc.*, 1965, **87**, 3826.

[4] J. H. Worrell and T. A. Jackman, *J. Amer. Chem. Soc.*, 1971, **93**, 1044.

[5] W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, 1970, **92**, 2677.

[6] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983.

[7] K. D. Kopple and R. R. Miller, *Proc. Chem., Soc.*, 1962, 306, *Inorg. Chem.*, 1963, **2**, 1204.

[8] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.

[9] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 793.

[10] D. L. Toppen and R. G. Linck, 'Reaction Mechanisms in Inorganic Chemistry', ed. M. L. Tobe, Medical and Technical Publishing Co. Ltd., London, in the press.