

## Double-bridging in Inner-sphere Electron Transfer Involving Chelates; Reduction of Bis(pentane-2,4-dionato)ethylenediaminecobalt(III) by Chromium(II)

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**Summary** The reduction of bis(pentane-2,4-dionato)ethylenediaminecobalt(III) by chromium(II) occurs by an inner-sphere path involving both single bridged and double bridged transition states in addition to the expected outer-sphere path.

THERE are only a few well characterised electron-transfer reactions in which a doubly bridged transition state has been shown to operate.<sup>1,2</sup> These involve two groups suitably positioned so as to bind simultaneously to the reductant, as in the reaction between *cis*-[(en)<sub>2</sub>Co(N<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and Cr<sup>2+</sup>.<sup>3</sup> The factors leading to double bridging are not well understood, nor predictable.

We report another case of double bridging which was quite unexpected. The reduction of [(en)Co(acac)<sub>2</sub>]<sup>+</sup> by Cr<sup>2+</sup> led to the production of [(H<sub>2</sub>O)<sub>4</sub>Cr(acac)]<sup>2+</sup> and [(H<sub>2</sub>O)<sub>2</sub>Cr(acac)<sub>2</sub>]<sup>+</sup> as well as the expected outer-sphere product [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. In view of these results, it appears that caution should be exercised in studying the redox chemistry of metal chelates. Not only are inner-sphere paths possible, as demonstrated earlier by Linck and Sullivan,<sup>3</sup> but also the possibility of a double bridged transition state, reported herein for the first time, must be considered. It should be emphasised that this may only unequivocally be established by product analysis studies which have not always been carried out in redox reactions involving metal chelates.

The overall rate constant for the reaction of Cr<sup>2+</sup> with [(en)Co(acac)<sub>2</sub>]<sup>+</sup> was 6.4 × 10<sup>-3</sup> l mol<sup>-1</sup> s<sup>-1</sup> [25 °C, μ 1.0 M (LiClO<sub>4</sub>)] and was independent of hydrogen ion concentration (0.1—0.8 M HClO<sub>4</sub>). Cation exchange chromatography<sup>4</sup> of reaction mixtures led to the isolation of 38% of [(H<sub>2</sub>O)<sub>4</sub>Cr(acac)]<sup>2+</sup> and 31% of [(H<sub>2</sub>O)<sub>2</sub>Cr(acac)<sub>2</sub>]<sup>+</sup> with the remaining Cr<sup>III</sup> being accounted for as [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>. To eliminate the possibility of the acac-Cr<sup>III</sup> products being formed as a result of substitution<sup>5</sup> of free acac on [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> (both formed *via* an outer-sphere reduction) a series of 'blank' product analyses was carried out. Free acac, [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>, and Cr<sup>2+</sup> were equilibrated for the same times and in the same proportions as in the reductions and were subjected to cation-exchange chromatography in an identical fashion. It was found that <5% of the mono-substituted Cr<sup>III</sup>-acac complex was formed by substitution and <1% of the disubstituted acac product was detected.

† en = ethylenediamine; acacH = pentane-2,4-dione.

‡ [(H<sub>2</sub>O)<sub>4</sub>Cr(acac)]<sup>2+</sup>: λ<sub>max</sub> (ε/l mol<sup>-1</sup> cm<sup>-1</sup>) 553 (26.8), 392 (209), 326 (8150), and 253 (4310) nm; [(H<sub>2</sub>O)<sub>2</sub>Cr(acac)<sub>2</sub>]<sup>+</sup>: λ<sub>max</sub> (ε/l mol<sup>-1</sup> cm<sup>-1</sup>) 553 (39), 388 (358), 328 (14,000), and 256 (9200).

§ N.m.r. measurements on [Co(acac)<sub>3</sub>] indicate that the methylene H peak at δ 5.81 observed in D<sub>2</sub>O disappears upon addition of acid. This was not observed for acidified D<sub>2</sub>O solutions of [(en)Co(acac)<sub>2</sub>]<sup>+</sup> and may indicate electronic and conformational changes due to protonation and exchange at the methylene carbon for [Co(acac)<sub>3</sub>] which is absent in the [(en)Co(acac)<sub>2</sub>]<sup>+</sup> case.

<sup>1</sup> R. Snellgrove and E. King, *J. Amer. Chem. Soc.*, 1962, **84**, 4609; R. Fraser, *ibid.*, 1963, **85**, 1747; J. Ward and A. Haim, *ibid.*, 1970, **92**, 475.

<sup>2</sup> A. Haim, *J. Amer. Chem. Soc.*, 1966, **88**, 2324.

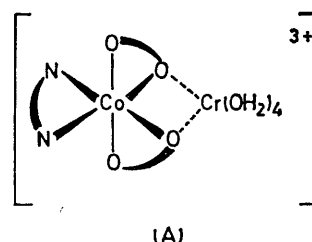
<sup>3</sup> R. Linck and J. Sullivan, *Inorg. Chem.*, 1967, **6**, 171.

<sup>4</sup> R. J. Balahura and N. A. Lewis, *Canad. J. Chem.*, 1975, **53**, 1154.

<sup>5</sup> D. Buckingham, J. Harrowfield, and A. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 7281, have shown that the reaction between acac and *cis*-[(en)<sub>2</sub>Co(OH<sub>2</sub>)(OH)]<sup>2+</sup> occurs by addition of the two co-ordinated oxygen atoms to the two carbonyl carbon atoms of acac and this type of mechanism could possibly provide a ready substitution on [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>.

<sup>6</sup> L. Orgel, Report of the Tenth Solvay Conference Brussels, 1956, p. 289.

In addition, [(H<sub>2</sub>O)<sub>4</sub>Cr(acac)]<sup>2+</sup> was equilibrated with free acac and Cr<sup>2+</sup> to check for the possibility of chromium(II)-catalysed formation of [(H<sub>2</sub>O)<sub>2</sub>Cr(acac)<sub>2</sub>]<sup>+</sup> but again <1% of disubstituted product was formed. Thus the two acac-containing Cr<sup>III</sup> products of the reduction must have resulted from inner-sphere paths. Formation of [(H<sub>2</sub>O)<sub>2</sub>Cr(acac)<sub>2</sub>]<sup>+</sup> can result from the dibridged transition state (A), where Cr<sup>2+</sup> must be bonded to two co-ordinated oxygen atoms from different acac rings. Rapid ring closure leading to the observed product is expected<sup>5</sup> after electron transfer. The [(H<sub>2</sub>O)<sub>4</sub>Cr(acac)]<sup>2+</sup> product can result either from attack of Cr<sup>2+</sup> at one co-ordinated oxygen followed by electron transfer with rapid ring closure or from simultaneous bonding of Cr<sup>2+</sup> to two oxygens of the same acac ring followed by electron transfer.



The reduction of the tris-acac complex, [Co(acac)<sub>3</sub>], by Cr<sup>2+</sup> occurs 66% by an outer-sphere path and 34% by a single bridging path.<sup>3</sup> It is surprising that no double bridging path was observed in this reaction since acac has a lower ligand field strength than en and on the basis of non-bridging ligand effects<sup>6</sup> such a path would be predicted. In [(en)Co(acac)<sub>2</sub>]<sup>+</sup> at least one en nitrogen atom is *trans* to one of the oxygen atoms bonded to the reductant and thus the dibridged path should be less favourable than for [Co(acac)<sub>3</sub>]. This is contrary to the observed behaviour. It may be that the conformation of the acac rings<sup>§</sup> is different in [(en)Co(acac)<sub>2</sub>]<sup>+</sup> than in the symmetrical [Co(acac)<sub>3</sub>] and that this in part determines whether a single- or a double-bridged path may operate.

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