SYNTHESIS OF CYCLOPENTADIENYL-ENE-1,2-DITHIOLATOCOBALT COMPLEXES AND COUPLED PROTON-ELECTRON TRANSFER IN A SUBSTITUTED QUINOXALINYL DERIVATIVE

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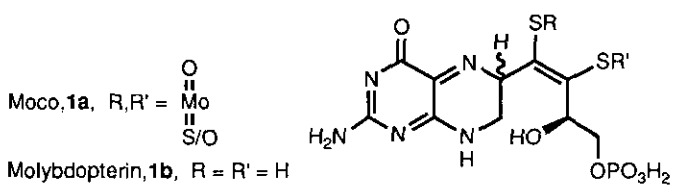
Abstract - A series of cyclopentadienyl-ene-1,2-dithiolatocobalt complexes, $[(\eta^5\text{-}C_5H_5)Co(S_2C_2RH)]$, has been prepared. The derivative in which quinoxalin-2-yl is bound to the dithiolene manifests novel electrochemical behaviour in acidic media which is consistent with a coupling of metal-centered electron addition to protonation of a pyrazine ring nitrogen.

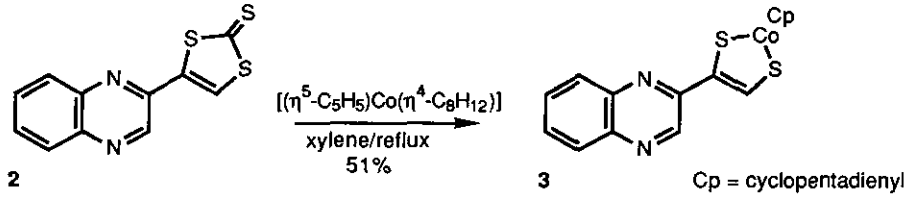
This communication is dedicated to Professor Edward C. Taylor, on the occasion of his 70th birthday, in acknowledgement of his major contributions to heterocyclic chemistry in general and to the study of pteridines in particular.

We are engaged on a series of investigations[1] related to the structure, synthesis, and mode of action of the cofactor of the oxomolybdoenzymes, **Moco**, in which molybdenum is complexed by a pteridine-containing unit, known as molybdopterin. Moco is extremely unstable hence its constitution[2] has been deduced from identifications of fully aromatic sulfur-containing pteridines, believed to be oxidative degradation products. However, there is evidence[3] that in Moco itself the pyrazine ring is in a reduced state, early views favouring a tetrahydro-level but the most recently reported work[4] suggesting that molybdopterin is a dihydropterin. A quinonoid tautomeric form (**1b**) was proposed implying partial structure (**1a**) for Moco, including absolute stereochemistry.[5] Of possible relevance to the mode of action of Moco, is the role of 5,6,7,8-tetrahydrobiopterin, the cofactor for monoamine-synthesising monooxygenases.[6]



It is clearly of importance that further comment be made on the state of oxidation of the pterin in Moco, in particular in so far as it relates to possible functional cooperativity between the metal center and the organic moiety. As a contribution to this goal we report here the syntheses of $[(\eta^5\text{-}C_5H_5)Co(S_2C_2RR')]$ complexes, which model the metal/sulfur/pteridine relationship in Moco, and electrochemical studies on one of these.

Cyclopentadienyl-ene-1,2-dithiolatocobalt complexes have been prepared previously;[7] $[(\eta^5\text{-}C_5H_5)Co(S_2C_2(CF_3)_2)]$,[8] $[(\eta^5\text{-}C_5H_5)Co(S_2C_2(CN)_2)]$,[9] and $[(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)]$[10] have been characterised by X-ray crystallography, and several compounds have been shown to undergo a reversible, one-electron reduction.[7d,11]



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Previous investigations in these laboratories[12] developed a synthetic route to cyclic 1,3-dithiole-2-thiones such as **2**. We have now shown that such compounds can be reacted with $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_8H_{12})]$ to prepare dithiolene complexes, for example $[(\eta^5\text{-}C_5H_5)Co\{S_2C_2H(\text{quinoxalin-2-yl})\}]$ (**3**) using the procedure developed by Siedle.[7b] Overall,

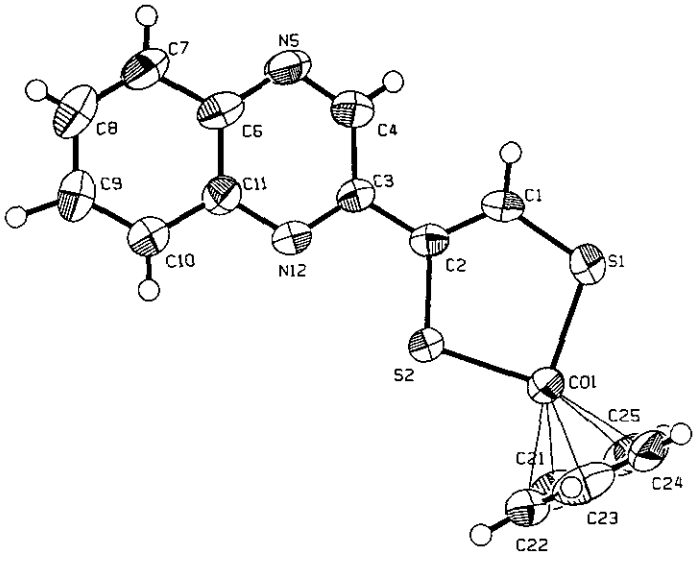


Figure 1 Arrangement of the non-hydrogen atoms of the molecule $[(\eta^5\text{-}C_5H_5)Co\{S_2C_2H(\text{quinoxalin-2-yl})\}]$

this approach is notable in that it permits the synthesis of [(η^5-C_5H_5)Co(S_2C_2RR')] complexes containing unsymmetrical dithiolenes. We have prepared a series of analogous complexes, with R=H, and R' =Ph; 2-, 3-, 4-pyridyl, and quinolin-2-yl; these compounds have been characterised by microanalysis, ^1H and ^{13}C nmr spectroscopy, and, in selected instances, by X-ray crystallography.

The crystal structure of **3** has been determined[13] and the geometry of the constituent molecules is depicted in Figure 1. The dimensions of the (η^5-C_5H_5)Co{S_2C_2} moiety are similar to the corresponding aspect in each of the three structurally characterised molecules of this type.[8-10] The five-membered cobalt-dithiolene ring is essentially planar as is the quinoxalin-2-yl group and these two units are nearly coplanar, being mutually disposed at an angle of only 10.6°. The ^1H nmr chemical shift of the hydrogen of the dithiolene group, at δ 9.74 ppm, is consistent with the presence of an aromatic current within the metal-containing-ring.[14]

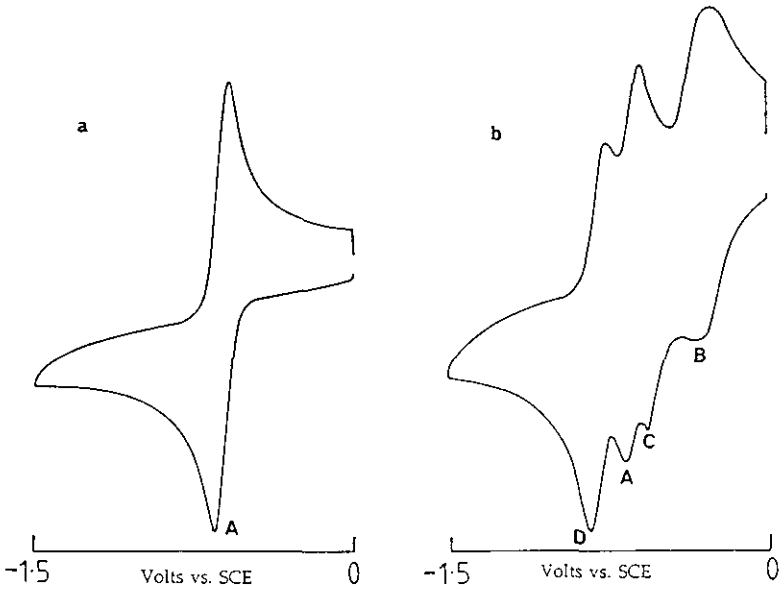
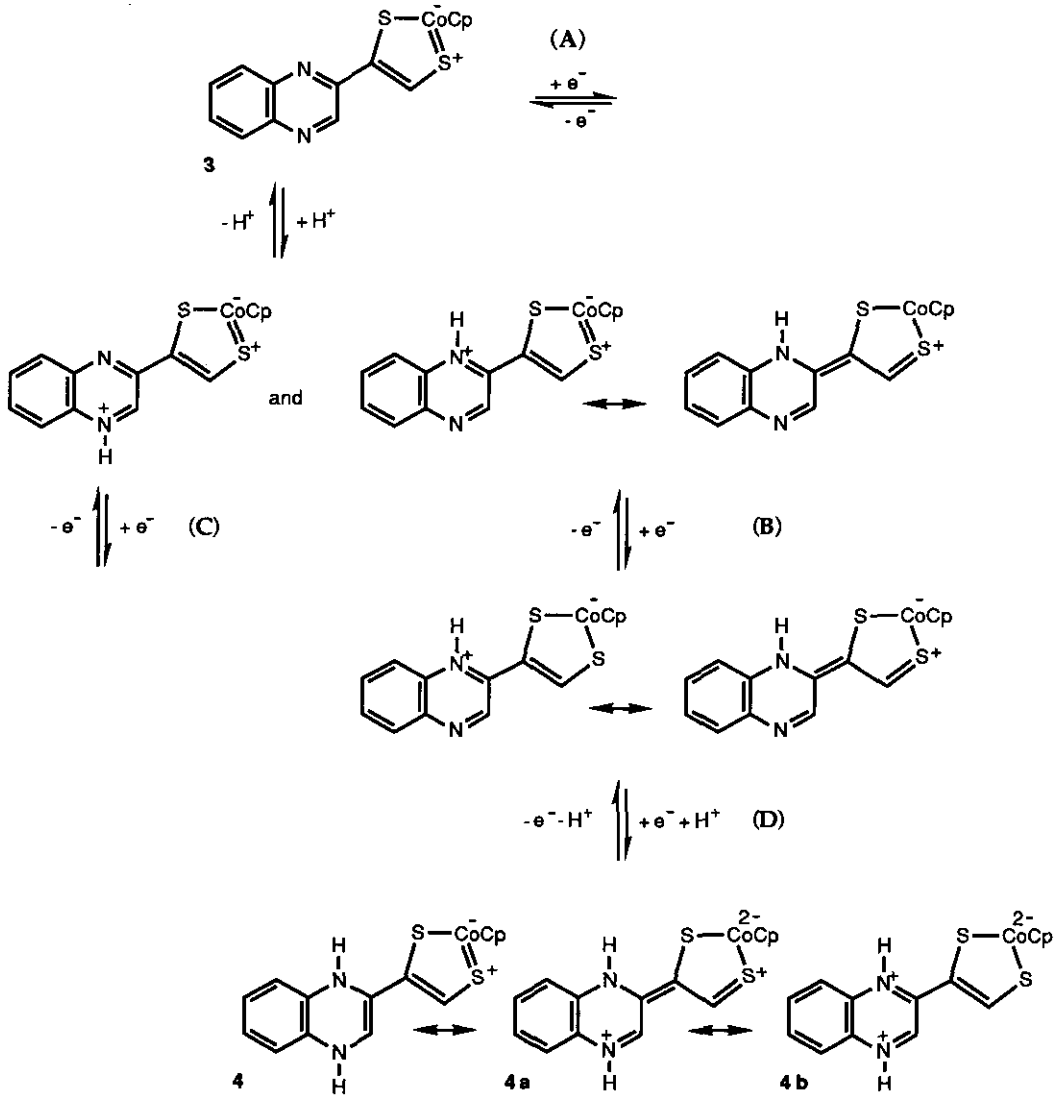


Figure 2 Cyclic voltammograms for the reduction of [(η^5-C_5H_5)Co{S_2CH(quinoxalin-2-yl)}] in MeCN with [*n*-Bu_4N][BF_4] as the electrolyte at a glassy carbon electrode and a scan rate of 100 mVs^{-1}; (a) compound alone; (b) compound with 1 equiv. CF_3CO_2H.

As with other compounds of this type,[7d,11] the blue complex (**3**) undergoes a reversible, one-electron reduction. However, the redox behaviour becomes dramatically different in the presence of protons (Figure 2). The appearance of up to four different reduction processes for **3** is unique amongst the molecules of this type which we have investigated. The process (**A**)

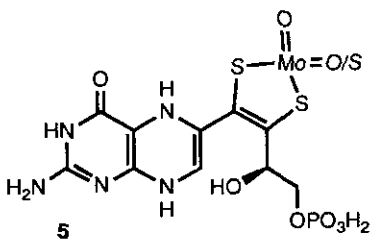
corresponds to the reduction of the neutral compound and we attribute the reductions (**B**) and (**C**) to the addition of an electron to the singly protonated species (Scheme); a similar shift to a less negative reduction potential is observed for $[(\eta^5\text{-}C_5H_5)Co\{S_2C_2HR\}]$ (R=2-, 3-, or 4-pyridyl) on addition of acid. The reduction (**D**) is considered to involve the addition of one further electron and one further proton to the previously reduced and protonated species. Thus, the final product of this $2e^-/2H^+$ addition, to which we ascribe structure (**4**) can be represented most



Scheme Suggested sequence for the reduction of $[(\eta^5\text{-}C_5H_5)Co\{S_2C_2H(quinoxalin\text{-}2\text{-}yl)\}]$ (**3**) in the presence of protons.

simply as involving overall reduction of the pyrazine ring to a dihydro-level, leaving the metal-dithiolene ring unchanged. Contributors (**4a**) and (**4b**) show how a 1,4-dihydro form would allow the maintenance of resonance interaction between the nitrogen atoms and the metal center.

Such behaviour, *viz.* "metal-centered" electronation coupled to the protonation of a ligand conjugated to the metal producing a new reduction process, is reminiscent of that observed for $[Mo(qdt)_3]^-$ (qdt=quinoxaline-2,3-dithiolate).[15] Furthermore, such a cooperativity augments the redox properties inherent to the metal center. Therefore, we propose that the coupling of the redox capability of the pterin to that of the molybdenum center *via* the dithiolene group confers *operational advantages* in respect of the two-electron redox changes catalysed by Moco. It would also imply that whatever the exact oxidation level of the pteridine in the native cofactor, there must be unbroken conjugation linking the metal center and the pteridine; dihydropteridine tautomers, (**5**) and (**6**), would fulfil this criterion where **1a** does not.



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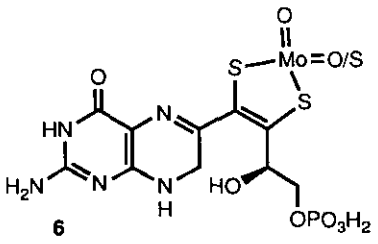

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ACKNOWLEDGEMENTS

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