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Cobalt(II) and Alkylcobalt(III) Complexes of N,N'-bis(2-thioformyl-2-phenylvinyl)trimethylenediamine. A Cobalt(II) Oxygen Carrier

ROBERT W. HAY, PAUL R. NORMAN and FIONA McLAREN

Chemistry Department, University of Stirling, Stirling, FK9 4LA, U.K.

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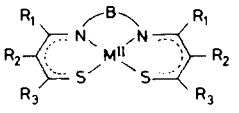
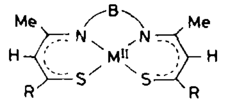
Introduction

In recent years there has been considerable interest in the chemistry of thioiminato ligands and their metal complexes [1–4]. The general structure of these complexes is shown in (I).

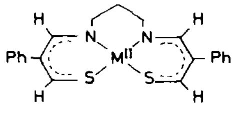


(I)

Cummings and coworkers [4] have studied a number of ligands of the thioiminato type and have shown that the cobalt(II) complexes act as oxygen carriers in non-aqueous solvents containing additional axial ligands such as pyridine, N,N'-dimethylformamide and N-methylimidazole. Previous work has been concerned with substituted derivatives of type (II). The present paper deals with the phenyl substituted complexes (III). It is of interest to study of the effect of the additional conjugation on the properties of the complexes.



(II)



(III)

Experimental

The 4-phenyl-1,2-dithiol-3-thione was prepared from sulphur and isopropylbenzene essentially as described by Fields [5]. This material was oxidised with peracetic acid in acetone and the perchlorate salt of the 4-phenyl-1,2-dithiolium cation isolated as described by Klingsberg [6]. Bis(2-thioformyl-2-phenylvinyl)trimethyldiamine was prepared essentially as previously described [7].

The cobalt(II) complex was prepared as follows. Cobalt(II) acetate tetrahydrate (1.25 g) was suspended in 50 cm^3 of methanol under an N_2 purge. The ligand (1.8 g) in chloroform (10 cm^3) was added and the solution stirred at 30 °C under N_2 for *ca.* 30 minutes. On cooling to 0 °C under N_2 the complex crystallised as dark brown microcrystals. Yield 2.2 g (70%). *Anal.* Calcd. for $C_{21}H_{20}N_2S_2Co$: C, 59.6; H, 4.8; N, 6.6. Found: C, 59.9; H, 4.9; N, 6.4%.

The nickel(II) complex was prepared similarly using nickel(II) acetate hexahydrate. Yield 83%. *Anal.* Calcd. for $C_{21}H_{20}N_2S_2Ni$: C, 59.6; H, 4.8; N, 6.6. Found: C, 59.7; H, 4.8; N, 6.7%.

Electrochemistry was carried out using a PAR170 electrochemistry system. Measurements were made using 1×10^{-3} *M* solutions of the cobalt complex in acetone with 0.1 *M* tetra n-butylammonium perchlorate as supporting electrolyte. All potentials are quoted *versus* and Ag/AgCl reference electrode. Magnetic susceptibilities were determined by the Faraday method. A standard Clarke oxygen electrode was used for the oxygen consumption measurements.

Results and Discussion

The visible spectrum of the cobalt(II) complex in acetone solution (under N_2) containing a trace of pyridine has bands at 487, 403 (sh) and 337 nm. On passing O_2 through the solution at –10 °C (ice–salt bath), there is a rapid visible colour change from brown to olive green, the resulting spectral changes are illustrated in Fig. 1. The band at 487 nm decreases

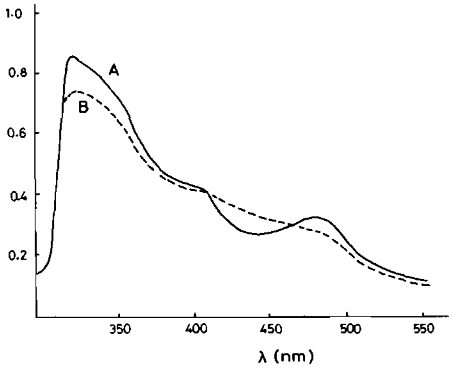


Fig. 1. Absorption spectrum of the cobalt(III) complex in acetone solution: (A) under N_2, (B) in the presence of O_2. The solution contains a trace of pyridine.

in intensity and becomes a shoulder on the main absorption band at 337 nm, in addition there is an increase in absorption at 440 nm. Passage of N_2 through the solution for *ca.* 45 minutes gives the initial spectrum. The oxygenation–deoxygenation cycles could be repeated eight to ten times before slight deviations from the two extreme spectra were noted. The spectral changes observed are similar to those reported by Carter *et al.* [8] for some structurally related cobalt(II) oxygen carriers.

The oxygenated complex was isolated by evaporation of the solvent, the infrared spectrum has new bands in the 1040–1140 cm^{-1} region which are absent in the deoxygenated complex. Crumbliss and Basolo [9] have reported bands in the region 1120–1140 cm^{-1} in the oxygen adducts of complexes of the type [BCo(acacen)] where B = N,N′-dimethylformamide or a substituted pyridine. Resonance Raman spectroscopy has also been used to detect a band at 1137 cm^{-1} assigned to ν_{O-O} in a mononuclear cobalt complex [10].

Oxygen uptake by the complex in acetone solution containing traces of pyridine was also confirmed by oxygen electrode measurements in the temperature range −15 to −20 °C. Solutions of acetone containing pyridine were saturated with O_2. Addition of the solid complex led to rapid decrease in the oxygen content of the solution.

The cobalt(II) complex has μ_{eff} = 2.49 BM at 20 °C consistent with the expected square planar stereochemistry on cobalt. Planar cobalt(II) complexes normally have magnetic moments in the range 2.4–2.8 BM as a result of the large orbital contribution [11].

The cobalt(II) complex in acetone solution gives two well defined reduction waves using DC polarography; for the first wave $E_{1/2} = -1.20$ v and a plot of E_{DME} *versus* log $(i/i_d - i)$ gives a straight line of gradient 96 mv. Various other techniques, Table I, were used to confirm a one electron reduction, the large gradient of 96 mv probably indicating DC maxima. Cyclic voltammetry on a hanging mercury drop, Fig. 2, satisfied the criteria for a fully reversible one electron reduction

$$Co^{II}(L) + e \rightleftharpoons Co^{I}(L)^{-}$$

The ratio of the cathodic peak current to the anodic peak current is *ca.* 1 and the peak separation is 60 mv. Although the reaction of Co(I) species with R_4N^+ ions has been noted [12],

$$Co^{I}(L)^{-} + N^{+}R_4 \longrightarrow Co^{II}(L) + NR_3 + R\cdot$$

at the sweep rates used (50–500 mVs^{-1}), Table II, the reaction of $Co^{I}(L)^{-}$ with the tetra-n-butyl ammonium ion is too slow to influence the electrode process characteristics.

TABLE I. Voltammetric Data for the Cobalt(II) Complex.

Technique	1st Reduction (v)	2nd Reduction (v)
AC/DME	−1.22 (Rev)	−1.80 (Irr)
CV/Pt	−1.20 (Rev)	−1.80 (Irr)
DC/DME	−1.20	−1.78
CV/HDME	−1.21 (Rev)	−1.78 (Irr)

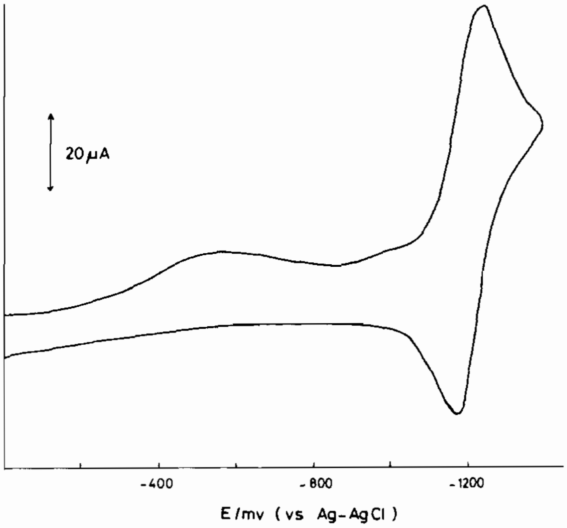


Fig. 2. Cyclic voltammogram on Pt of 1.0 m*M* solution of the cobalt(II) complex in acetone with 0.1 *M* $(n\text{-butyl})_4N^+ClO_4^-$ as the supporting electrolyte. Scan rate 200 mV/sec. The first scan is shown.

TABLE II. Cyclic Voltammetry on Pt.[a]

Scan Rate (ν) (mv/s)	$\nu^{1/2}$	Ip(c) (µA)	Ip(a) (µA)	Ip(c)/Ip(a)	ΔEp (mv)	½Ep (v)
50	7.07	30.7	27	1.13	65	−1.21
100	10.0	45	37	1.21	65	−1.21
200	14.14	60	52	1.15	70	−1.20
500	22.36	86	76	1.13	70	−1.21

[a] 1.0 m*M* cobalt(II) complex in acetone and 0.1 *M* TBAP. Switching potential constant at −1.65 v, Ag/AgCl reference electrode.

The second reduction at ½Ep = −1.78 v by cyclic voltammetry on a HMDE and on Pt has no re-oxidation wave and represents an irreversible electron transfer.

Addition of one molar equivalent of methyl iodide to the cobalt(II) complex in acetone leads to a shift in the half wave potential for the first reduction. Cyclic voltammetry on Pt establishes that addition of methyl iodide leads to a decrease in i_{ap}, the reoxidation wave for the first reduction, while the second reduction step does not occur. The electrochemical measurements are consistent with a rapid reaction of the cobalt(I) species with methyl iodide to give the alkylcobalt(III) species

$$\mathrm{Co^{I}(L)^{-} + MeI \longrightarrow Me{-}Co^{III}(L) + I^{-}}$$

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