Some Cobalt Complexes of Binucleating Schiff Base Ligands

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The cobalt(II) complexes of three binucleating ligands have been prepared and characterized. The chemistry of these complexes has been examined, largely reactions in methanol solution. The dicobalt-(II) complexes are readily oxidized to the di-cobalt-(III) analogs, and these in turn are re-reduced to the parent complexes. One organometallic derivative was prepared, the $(CH_3Co)_2$ complex of the ligand 5-Bu^{t}sal$_4$bz. It was characterized by its reaction with mercury(II) and its photodecomposition to the di-cobalt(II) complex in the absence of oxygen and to di-cobalt(III) when oxygen is present.

Introduction

Bimetallic complexes constitute an interesting area for study in that the chemistry and reactivity of the metals may, in some circumstances, differ quite markedly from the mononuclear analogs. In view of a recent review of the field [1] it is not necessary to give extensive background information. Our intention was to prepare and study dicobalt complexes which would be analogs of the well-known complexes of the mononucleating ligands sal$_2$enH$_2$(I) and sal$_2$phenH$_2$(II), the bimetallic complexes consisting of two such coplanar units [2]. The 'link' between the two is the 1,2,4,5-tetraamino benzene unit, shown by magnetic studies [3, 4] to be effective in promoting metal–metal interactions. The particular binucleating ligands whose cobalt complexes have been examined here are sal$_4$bzH$_4$(III) (this ligand is also known [5] as TSAB) and analogs in which *tert*-butyl and sulfonate groups are substituted in the 5-positions of salicylaldehyde (IV and V), such substitution intended to promote greater solubility. The structural formulas shown for the ligands do not specify the individual derivatives as to the oxidation state of the cobalt, its axial ligands, and the overall ionic charge. Related complexes, primarily of Cu(II), Ni(II), and Co(II), have been studied extensively by Merrell and coworkers [5–8]. The particular chemistry we have examined concerns the formation of methylcobalt complexes and related organometallics and the oxidation–reduction processes between

III   R = H
IV   R = tert–Bu
V   R = SO$_3$
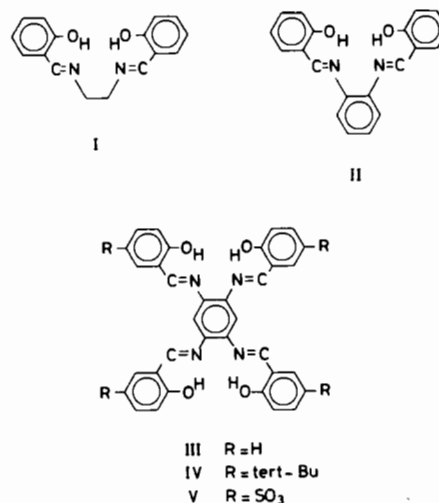
the $[Co^{II}]_2$ and $[Co^{III}]_2$ states along with considerations of a mixed-valence $[Co^{II}Co^{III}]$ form.

Experimental

Ligands

The binucleating ligands shown in Structures III-V were prepared from 1,2,4,5-tetraaminobenzene tetrahydrochloride (Aldrich). This compound was neutralized with sodium methoxide freshly prepared from the metal and anhydrous methanol (commercial sodium methoxide proved unsatisfactory), giving a tetraamine which was then immediately condensed with salicylaldehyde or a derivative.

Sal$_4$bzH$_4$

Sodium methoxide was added to a stirred suspension of the tetraamine (0.95 g, 3.3 mmol) in 100 mL dry methanol under nitrogen until reaction was complete, resulting in a final yellow solution. Salicylaldehyde (1.61 g, 13.2 mmol) was then immediately added dropwise to the warm solution. The solution was refluxed overnight, the orange solid filtered, washed several times with methanol and ether, and air dried. (Yield, 90%, mp 270–290 °C dec). The ligand is insoluble in most solvents but small quanti-

TABLE I. Electronic Spectra of Ligands and of Cobalt Complexes.

Compound	Solvent	λ_{max}/nm $(\log_{10} \Sigma/M^{-1}\ cm^{-1})$
sal$_4$bzH$_4$, *III*	DMSO	396(4.44), 353(4.48)
(Co^{II})$_2$(sal$_4$bz)	DMSO	475(4.78), 322(4.78)
(Co^{III})$_2$(sal$_4$bz)$^{2+}$	DMSO	520(–), 491(–), 331
5-Bu^{t}sal$_4$bzH$_4$, *IV*	THF	398(4.57), 366(4.58), 277(4.49)
(Co^{II})$_2$(5-Bu^{t}sal$_4$bz)$^{2+}$	methanol	~450(~4.5), 328(~4.6)
(Co^{III})$_2$(5-Bu^{t}sal$_4$bz)$^{2+}$	methanol	525(4.52), 491(4.53), 344(4.54), 258(4.85)
(Co^{II})$_2$(5-SO$_3$sal$_4$bz)$^{4-}$	water	416(4.69), 310(4.56)
(Co^{III})$_2$(5-SO$_3$sal$_4$bz)$^{2-}$	water	498(4.63), 467(4.62), 334(4.56), 262(5.04)

ties could be recrystallized from chloroform. *Anal.* Calcd for sal$_4$bzH$_4$·1.5CHCl$_3$, C$_{34}$H$_{26}$N$_4$O$_4$·1.5CHCl$_3$: C, 55.66; H, 3.57; N, 7.64. Found: C, 56.18; H, 3.69; N, 8.08.

5-Bu^{t}sal$_4$bzH$_4$

The procedure is similar to that given above, performed on twice the scale. The aldehyde was prepared using the Duff reaction [9]: anhydrous glycerol (150 g) and boric acid (35 g) were heated to 170 °C in a 3-necked, 1 L rb flask for 1 hr, then cooled to 160 °C, and 25 g each of p-tert-butylphenol and hexamethylenetetraamine were added rapidly in alternating portions with external cooling to keep T < 190 °C. The solution was stirred for 5–7 min (only) then cooled to 100–110 °C and H$_2$SO$_4$ (100 mL; 4 *M*) added. The solution was steam distilled, and 1–2 L of distillate collected, extracted with ether, and the extract allowed to stand 16 h over anhydrous calcium chloride. The ether layer was filtered then evaporated, producing a yellow oil which was vacuum distilled to yield the 5-tert-butylsalicylaldehyde, 57–58.5 °C/0.1 torr. This material, when added to the tetramine, produced ligand IV as an orange precipitate which was recrystallized from boiling chloroform. *Anal.* Calcd for 5-Bu^{t}sal$_4$bzH$_4$, C$_{50}$H$_{58}$N$_4$O$_4$: C, 77.09; H, 7.50; N, 7.19. Found: C, 76.23; H, 7.56; N, 7.62. ^{1}H NMR, 100 MHz (CDCl$_3$): δ 1.33 (s, 36H, Bu^t), δ 7.08, 7.42 (m, 14 H, arom), δ 8.76 (s, 4H, –CH=N), 12.64 (s, 4H, OH). Mass Spec. m/e 779(M$^+$).

5-SO$_3$sal$_4$bzH$_4^{4-}$

This ligand was prepared from 5-sulfosalicylaldehyde [10] and was not isolated but directly converted to the cobalt complex.

Cobalt Complexes

The cobalt complex of ligand III was prepared by placing a small quantity of the ligand (~0.4 mmol) in a glass-fritted extraction thimble of a Soxhlet apparatus containing cobalt(II) acetate (0.9 mmol) in THF. The system was kept under nitrogen while being extracted for several days. The product, Co$_2$-(sal$_4$bz), was obtained as a dark brown powder which was filtered under nitrogen. It is so very insoluble in all solvents that little further work was done using this complex.

The complex Co$_2$(5-Bu^{t}sal$_4$bz) was prepared by adding an ethanolic solution of cobalt(II) acetate-tetrahydrate (3.2 mmol in 100 mL) dropwise to a warmed chloroform solution of the ligand (1.6 mmol in 800 mL) under nitrogen. The complex precipitated after some hours and was then allowed to stir overnight, filtered (the solid, unlike its solutions, is not particularly oxygen sensitive), and dried at 100 °C for 10 hr. *Anal.* Calcd for C$_{50}$H$_{60}$N$_4$O$_8$Co$_2$: C, 62.24; H, 6.34; N, 5.81; Co, 12.2. Found: C, 62.65; H, 6.00; N, 6.32; Co, 12.3.

The complex Co$_2$(5-SO$_3$sal$_4$bz)$^{4-}$ was prepared by adding cobalt(II) acetate in DMSO to a solution of freshly prepared ligand V in DMSO/MeOH. The solution was stirred 18 hr, the precipitate filtered, washed with ethanol and ether, and air dried.

Methylcobalt Complex

The only organometallic derivative prepared was (CH$_3$Co)$_2$(5-Bu^{t}sal$_4$bz). Sodium borohydride was added to a solution of the parent (Co^{II})$_2$ complex in methanol under nitrogen producing a light yellow solution. An excess of methyl iodide was added, and the flask sealed and stirred for several hours in the dark. The solution, now quite dark, was extracted with methylene chloride after adding water to the methanol layer. The desired complex, a brown solid subject to photodecomposition particularly in solution, was isolated by removal of the solvent. It could be further purified from any contaminants, usually the (Co^{III})$_2$ complex, by column chromato-

graphy on Sephadex LH-20 and elution with methylene chloride–methanol (10:1).

Measurements

Complexes were characterized, and their reactions studied, by UV–visible spectrophotometry, conventional (Cary Model 219) and stopped-flow (Durrum Model D-110) instruments being used. Table I gives spectral data for the ligands and complexes. Nmr data were obtained with a Varian HA-100 spectrometer; ir spectra were determined using a Beckman 4820 instrument.

Results

Oxidation-Reduction Reactions

The complexes prepared were the $(Co^{II})_2$ derivatives; upon dissolution of $(Co^{II})_2(5\text{-}Bu^t sal_4 bz)$ in methanol partial oxidation was usually observed even when air was carefully excluded. In contrast, no oxidation of the cobalt(II) complex was seen in non-coordinating solvents such as methylene chloride or chloroform. Addition of a potential ligand such as pyridine resulted in rapid reaction of the Co(II) complex with oxygen.

In this work it was necessary to employ methanol for most reactions, and it was generally more convenient to prepare solutions of the $(Co^{III})_2$ complex by dissolving the solid in aerated methanol, then forming the $(Co^{II})_2$ complex by reduction with chromium(II) chloride solution (or with hydrogen over Adams' catalyst) after prolonged deaeration with Cr^{2+}-scrubbed nitrogen. The bulk of our studies of the solution chemistry was carried out in methanol with complexes of the t-butyl ligand IV, since complexes of the parent ligand III are soluble only at $<10^{-5}$ *M* levels, and complexes of the sulfonated ligand are not easily purified and appear to undergo hydrolytic decomposition when heated.

We formulate the 'completely oxidized' products, as noted above, as a cobalt(III) complex, abbreviated $(Co^{III})_2$, and not as an oxygen adduct. The same complex, as judged by its UV–visible spectrum, is produced by reaction of $(Co^{II})_2$ not only with molecular oxygen, but also with $Co(NH_3)_5Br^{2+}$ and hydrogen peroxide.

Solutions of the $(Co^{III})_2$ complex, prepared by air oxidation of the $(Co^{II})_2$ solid dissolved in methanol, reacted rapidly (within the mixing time) with Cr^{2+}. Accompanying the reduction were parallel decreases in the intensities of the double absorption band associated with $(Co^{III})_2$, at 496 and 523 nm, and an intensification of the absorption band of $(Co^{II})_2$ at 450 nm. This is illustrated in Fig. 1. Table I summarizes spectral data. Throughout this region of concentration, isosbestic points were maintained at least approximately at 377 and 479 nm. The
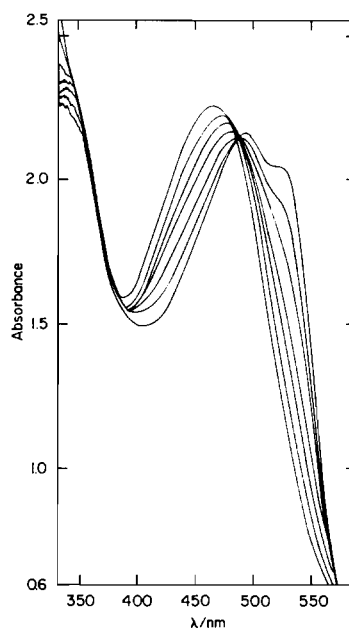

Fig. 1. Spectral changes noted upon reaction of 6.2×10^{-5} M $(Co^{III})_2(5\text{-}Bu^t sal_4 ba)^{2+}$, formed by air oxidation of the cobalt(II) complex in methanol, with successive increments of chromium(II) chloride. The final spectrum of $(Co^{II})_2(5\text{-}Bu^t sal_4 bz)$, with a maximum centered at 450 nm, was formed after addition of a 2:1 mol ratio of Cr(II) to $(Co^{III})_2$. The Cr(II) was present in aqueous solution, but the final solution is >97% methanol.

absorption intensity of the $(Co^{II})_2$ product attains a maximum at a ratio $2Cr^{2+}:1(Co^{III})_2$, consistent with the net reaction

$$2Cr^{2+} + (Co^{III})_2 = 2Cr^{3+} + (Co^{II})_2 \qquad (1)$$
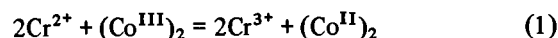
Because isosbestic points are maintained, we conclude that either the following disproportionation equilibrium lies far to the right, or (more likely), that the mixed-valence complex, (Co^{II}, Co^{III}) has a visible absorption spectrum which is the exact average of its two components

$$2(Co^{II}, Co^{III}) = (Co^{II})_2 + (Co^{III})_2 \qquad (2)$$
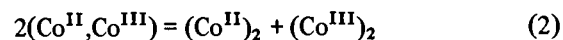
Addition of Cr^{2+} beyond the 2:1 point resulted in a decrease of intensity of the $(Co^{II})_2$ absorption band at 450 nm. This subsequent reaction appears to be irreversible in that reagents such as $Co(NH_3)_5$-Br^{2+} failed to restore the spectrum of the parent $(Co^{III})_2$ complex. It thus appears that excess Cr^{2+} results in ligand reduction, a process likely to occur irreversibly, although we have not explored the chemistry further. Similar results were obtained in the presence of 0.01–0.02 *M* pyridine, although the cobalt(III) spectrum is altered somewhat.

The sulfonated complex, $(Co^{III})_2(5\text{-}SO_3sal_4bz)^{2-}$, also reacted with Cr^{2+} in aqueous solution to produce the $(Co^{II})_2$ complex. Similar spectral changes accompanied the reaction and again a stoichiometric titration gave results consistent with eq. 1. It should be noted that aqueous solutions of the $(Co^{III})_2$ complex show <3% decomposition in water at 25 °C over 24 hours. This finding is consistent with a report that aqueous solutions of $Cu^{II}(5\text{-}SO_3sal_2en)$ are stable [11]. In contrast, Ni(II) and Cu(II) complexes of $5\text{-}SO_3sal_4bz$ are reported to be unstable in water [5].
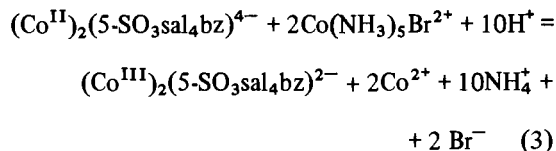
Preliminary kinetic studies of reaction 1 for the $(Co^{III})_2(5\text{-}Bu^tsal_4bz)^{2+}$ complex showed that the reaction occurred on a very fast stopped-flow scale (~10 ms), but a quantitative kinetic study was prevented by several practical factors such as the difficulty of keeping dilute Cr^{2+} in methanol at pH > 3 (needed to prevent the $(Co^{II})_2$ product from decomposing), as well as competition between reaction 1 and ligand reduction, which proved important with excess Cr^{2+}. Some studies of the reaction of $(Co^{III})_2(5\text{-}SO_3sal_4bz)^{2-}$ with Cr^{2+} were also carried out, now in aqueous acetic acid-acetate solution. Excess Cr^{2+} caused competing ligand reduction, and experiments under second-order conditions gave $k \sim 10^6 \ M^{-1} \ s^{-1}$ (pH 4.3) and $k \sim 10^7 \ M^{-1} \ s^{-1}$ (pH 6.0).

Molecular hydrogen over PtO_2 (Adams' catalyst) also reduces $(Co^{III})_2(5\text{-}Bu^tsal_4bz)$ to give a $(Co^{II})_2$ complex having a spectrum which matches that from the Cr(II) reduction. (To filter the finely-divided catalyst from these very dilute solutions without exposure to air, a millipore filter arrangement with Luer-type syringe fittings proved convenient.)

Provided an excess of chromium(II) had not been added to the air-oxidized solution containing $(Co^{III})_2$ $(5\text{-}Bu^t sal_4bz)$, the $(Co^{II})_2$ complex so formed could be re-oxidized. Also, $(Co^{II})_2$ solutions prepared by hydrogen reduction behaved identically. Several oxidants effected this change: O_2, H_2O_2, $(NH_3)_5\text{-}CoCl^{2+}$, $(NH_3)_5CoBr^{2+}$, and Ce(IV). In some cases recovery of $(Co^{III})_2$ was incomplete; for example, the $(Co^{II})_2$ complex is unstable to high $[H^+]$, forming Co^{2+} and thus the cerium(IV) reagent containing sulfuric acid regenerates the $(Co^{III})_2$ absorption spectrum but at reduced intensity. Also, both O_2 and H_2O_2 give product spectra in which the 'double-peak' characteristic of $(Co^{III})_2$, at 496 and 532 nm, is less well resolved than before the cycle of oxidation (original dissolution in aerated methanol), reduction (with $CrCl_2$ or H_2), and re-oxidation.

The oxidants most successful in restoring the $(Co^{III})_2$ spectrum are $Co(NH_3)_5X^{2+}$ (X = Br, Cl), the bromo complex appearing to react in several stages, but finally requiring some 10–30 min to reach completion and the chloro even longer. In the case of $(Co^{II})_2(5\text{-}SO_3sal_4bz)^{4-}$ the oxidation with $Cr(NH_3)_5\text{-}Br^{2+}$ occurred rapidly in water with an exact 1:2

stoichiometry (eq. 3). We assume a similar stoichiometry for the reaction of $(Co^{II})_2(5\text{-}Bu^t_3sal_4bz)$ with $Co(NH_3)_5Br^{2+}$ but its relative slowness permitted only a qualitative confirmation.

$$(Co^{II})_2(5\text{-}SO_3sal_4bz)^{4-} + 2Co(NH_3)_5Br^{2+} + 10H^+ =$$

$$(Co^{III})_2(5\text{-}SO_3sal_4bz)^{2-} + 2Co^{2+} + 10NH_4^+ +$$

$$+ 2 \ Br^- \quad (3)$$

Reaction of $(Co^{II})_2(5\text{-}Bu^tsal_4bz)$ with hydrogen peroxide appeared to occur in several stages, some at stopped-flow rates and others easily followed by conventional spectrophotometry. When $(Co^{II})_2(5\text{-}SO_3\text{-}sal_4bz)$ was reacted with a 10-fold excess of H_2O_2, data were obtained suggesting an autocatalytic reaction. The processes thus appeared too complicated for meaningful kinetic study at this stage of the work.
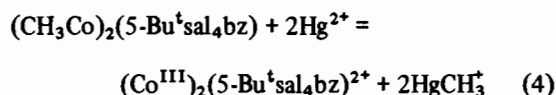
Organocobalt Complexes

A methanolic solution of $(Co^{III})_2(5\text{-}Bu^tsal_4bz)$ was treated with excess sodium borohydride. The red solution quickly turned a pale yellow, visually as well as spectroscopically quite different from the brown $(Co^{II})_2$. The cobalt species present is probably not a cobalt(I) complex; it exhibits neither the absorption spectrum nor the chemical reactivity expected for cobalt(I). We might simply designate it as the 'reduced complex', although we recognize that it may in fact be a hydridocobalt complex, the conjugate acid of the Co(I) species. It reacts cleanly with Cu^{2+} to restore a spectrum similar to that of $(Co^{II})_2$, but with λ_{max} 420 rather than 450 nm. This suggests the reduced species may not have suffered ligand reduction considering the reversibility and the rapidity with which it is converted to $(Co^{II})_2$ by an electron-transfer reagent. Variable results were obtained from experiments to determine the quantity of Cu^{2+} required to form $(Co^{II})_2$ completely, even with acetone added to quench excess borohydride ions.

The reduced complex reacts *slowly* with methyl iodide; in contrast, the parent $(Co^{II})_2$ is unreactive. From this reaction a product is obtained having characteristics and reactions expected for the methyl-cobalt complex $(CH_3Co)_2(5\text{-}Bu^tsal_4bz)$. The procedure used is the following (note the small scale necessitated by low solubility limits). Sodium borohydride (~5 mg, 0.13 mmol) was added to a solution of $Co^{II}(5\text{-}Bu^tsal_4bz)$ (30 mg, 0.03 mmol) in 250 mL methanol under nitrogen, followed by methyl iodide (0.1 mL, 1.6 mmol). The brown solution was stirred for several hours while protected from light. Water was added to the methanol, which was then extracted with methylene chloride (~100 ml). Solvent was removed from the latter layer, yielding a dark brown

solid which could be purified on Sephadex LH-20. The desired product was eluted with 10:1 CH_2Cl_2/ CH_3OH, and isolated as a brown crystalline solid (*ca.* 10 mg), while a small pink band of the $(Co^{III})_2$ complex remained at the top of the column. The organocobalt complex gave a ^1H nmr spectrum which showed resonances for all the ligand protons in the complex. The small quantity available and its low solubility did not permit the $Co–CH_3$ protons to be detected, however. It is important to note that no ligand reduction was evident.

This complex reacts rapidly with Hg^{2+} generating a product identified spectrophotometrically as $(Co^{III})_2(5-Bu^tsal_4bz)^{2+}$; the other product is presumed to be $HgCH_3^+$, but this was not identified owing to the small quantities involved. A spectrophotometric titration with Hg^{2+} indicated a 1:2 stoichiometry in accord with the overall equation

$$(CH_3Co)_2(5-Bu^tsal_4bz) + 2Hg^{2+} =$$

$$(Co^{III})_2(5-Bu^tsal_4bz)^{2+} + 2HgCH_3^+ \quad (4)$$

This reaction bears a close resemblance to those of similar mononuclear organocobalt complexes [11]. Some kinetics experiments were carried out under concentration conditions employing excess mercury-(II). The reaction followed pseudo-first-order kinetics under these conditions. Data obtained in methanol containing 0.1 M nitric acid at 25 °C are as follows:

$10^4[Hg^{2+}]/M$	k_{obs}/s^{-1}	$10^{-3}k_{obs}[Hg^{2+}]^{-1}/M^{-1}\ s^{-1}$
1.05	0.29	2.7
2.10	0.52	2.5
4.20	0.86	2.1

The quotient $k_{obs}/[Hg^{2+}]$ shows a slight trend with $[Hg^{2+}]$, decreasing with increasing mercury(II). Although mechanisms involving some preassociation could be formulated to account for this trend, a more conservative approach (considering the limited accuracy of but three experiments) is to cite the approximate adherence to a second-order kinetic equation.

The organocobalt complex is insensitive to oxygen in the dark. In the presence of light, however, particularly if oxygen is present, the complex proved photosensitive, decomposing to form the $(Co^{III})_2$ complex and cleaving the methyl–cobalt bond. Figure 2 shows the spectral changes observed. If O_2 was excluded the spectral changes when photolyzed indicated a loss of $(CH_3–Co)_2$, but formation of a $(Co^{II})_2$-like spectrum.

Several attempts were made to prepare the corresponding ethylcobalt complex, but no apparent reaction with ethyl iodide was found. This strengthens our argument that the 'reduced com-
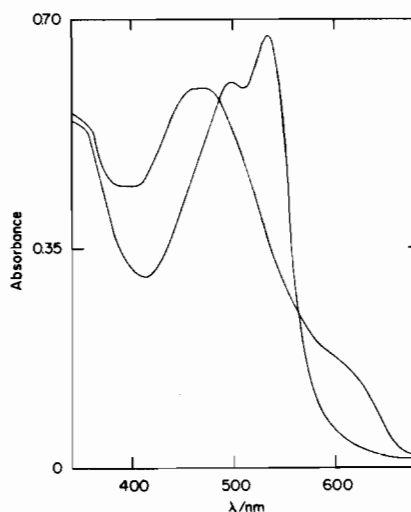

Fig. 2. UV–visible spectrum in methanol of 3.0 × 10^{-5} M $(CH_3Co)_2(5-Bu^tsal_4bz)$ with λ_{max} ~470 nm and of the $(Co^{III})_2$ product resulting from its photodecomposition in the presence of air.

plex' from borohydride may be the hydrido complex $(HCo)_2(5-Bu^tsal_4bz)$, and only methyl iodide reacts sufficiently rapidly with the minute trace of its conjugate base, the dinuclear cobalt(I) complex, to yield an organometallic derivative.

Conclusions

Although it proved feasible to study only a limited amount of their chemistry, and quantitative data are scarce, it seems evident that the dinuclear cobalt complexes examined are not remarkably different from their mononuclear analogs. To the extent that we can recognize, the reactions that occur, the spectral changes that accompany these reactions, and indeed even the results from the reaction kinetics give little evidence of there being a degree of interaction between the two metals which is manifested in this manner. Rather, it appears that any 'mixed valence' species has the average properties of its constituents, and that the dinuclear organocobalt complex is a close analog of mononuclear compounds in its chemistry and reactivity.

Acknowledgement

References

1 S. E. Groh, *Israel J. Chem.*, *15*, 277 (1976/1977).
2 U. T. Mueller-Westerhoff, *Advances in Chemistry Lines, 150*, 'Inorganic Compounds with Unusual Properties', R. B. King, Ed., *Amer. Chem. Soc.*, Washington, DC (1971).
3 E. F. Hasty, T. L. Colburn, and D. N. Hendrickson, *Inorg. Chem.*, *12*, 2414 (1973).
4 T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, *17*, 2636 (1978).
5 P. H. Merrell and M. Abrams, *Inorg. Chim. Acta, 32*, 93 (1979).
6 P. H. Merrell and L. J. Maheu, *Inorg. Chim. Acta, 28*, 47 (1978).
7 P. H. Merrell and R. A. Osgood, *Inorg. Chim. Acta, 14*, L33 (1975).
8 P. H. Merrell, *Inorg. Chim. Acta, 32*, 99 (1979).
9 J. C. Duff, *J. Chem Soc.*, 547 (1941).
10 G. Kirker, submitted for publication.
11 H. Elias and G. Kohler, *Inorg. Chim. Acta, 34*, L215 (1979).
12 J. H. Espenson, W. R. Bushey, and M. E. Chmieliewski, *Inorg. Chem.*, *14*, 1302 (1975).