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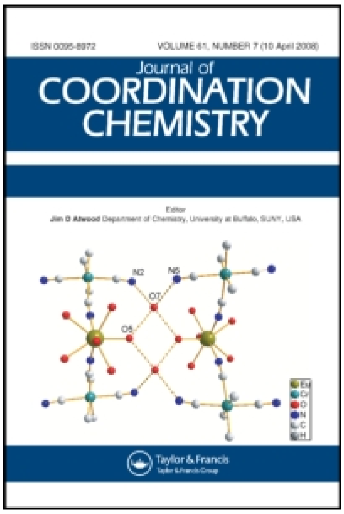

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COBALT(H) COMPLEXES OF SHORT CHAIN PENTADENTATE LIGANDS AND THEIR REACTION WITH DIOXYGEN

S. R. Edmondson[a]; R. H. Niswander[a]; L. T. Taylor[a]
[a] The Department of Chemistry, Virginia Polytechnic Institute and State University, Blackburg, Virginia, U.S.A.

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COBALT(II) COMPLEXES OF SHORT CHAIN PENTADENTATE LIGANDS AND THEIR REACTION WITH DIOXYGEN

S. R. EDMONDSON, R. H. NISWANDER and L. T. TAYLOR

The Department of Chemistry, Virginia Polytechnic Institute and State University, Blackburg, Virginia 24061, U.S.A.

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Cobalt(II) complexes have been prepared with ligands derived from salicylaldehyde (or a substituted salicylaldehyde) and bis(2-aminoethyl)amine. These compounds are designated Co(RSALDIEN) and represent an unusual situation in which one of the donor atoms is not coordinated to the metal. As a result, tetrahedral complexes are observed which are very hygroscopic. These compounds also react with dioxygen to produce an irreversible paramagnetic dioxygen adduct. It is believed that the imine group remains uncoordinated in the oxygenated complex, thus giving the first example of a five-coordinate cobalt dioxygen complex.

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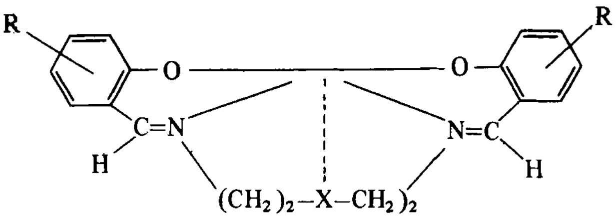
INTRODUCTION

Previous work in this laboratory has resulted in the preparation and characterization of a group of nickel(II) complexes shown in Structure I.[1,2]



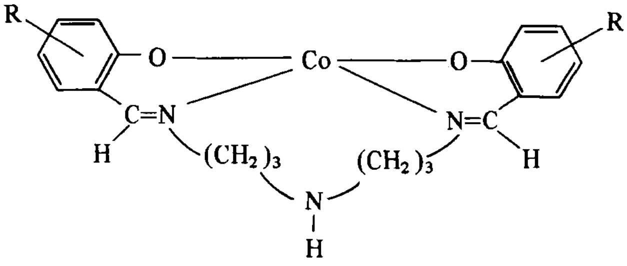
Complex	*X*
Ni(RSALDIEN)	N–H
Ni(RSALDAES)	S

R = H, 5-Br, 3-CH_3O, 5-CH_3, 3-i-C_3H_7

STRUCTURE I

Compounds wherein X=S were postulated to have five-coordinate structures with anomolous magnetic moments. Spectral and magnetic data supported a square planar or an axially perturbed five-coordinate geometry for X=N–H. A report dealing with cobalt(II) complexes, Co(RSALDAES), has also been published.[3] These compounds were found to be four-coordinate with high spin tetrahedral configurations. The adoption of a pseudo-tetrahedral structure instead of a square planar or five-coordinate structure as observed in the nickel(II) case supports the crystal field idea that for flexible polydentate ligands, cobalt(II) forms more stable tetrahedral complexes than nickel(II). No doubt the low affinity of thioethers for first row metals contributes to this observation.[4] It is therefore interesting to compare cobalt(II) complexes of RSALDAES with ligands such as RSALDIEN which incorporate a different type of central donor.

Cobalt(II) complexes of similar type ligands, RSALDPT (Structure II), form high spin distorted trigonal bipyramidal five-coordinate complexes,[5] but these compounds have a longer chain joining the secondary amine and imine nitrogens.



Co(RSALDPT)

STRUCTURE II

These compounds have also been found to react with dioxygen to form six-coordinate adducts.[6,7] Dioxygen reactivity varied depending on the aromatic ring and central nitrogen donor substituents. Electron donating groups on the salicylaldehyde moiety enhanced

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reaction with dioxygen. Alkyl and aryl groups attached to the central donor inhibited oxygen up-take.[9] Co(RSALDPT) yielded isolable diamagnetic 2:1 μ-peroxo complexes from solution. In solution the dimeric peroxo complex is in equilibrium with esr active 1:1 superoxo species. The present report deals with cobalt(II) complexes formed from RSALDIEN. We have found dramatic differences in these compounds, both in the structure of the cobalt(II) precursors and in their reactivity toward oxygen.

EXPERIMENTAL

All chemicals used in the preparation of these cobalt complexes were reagent grade. 3-Methoxysalicylaldehyde and bis(2-aminoethyl)amine were purified by vacuum distillation to insure their purity.

Preparation of Co(SALDIEN)·2H_2O To a refluxing solution prepared by dissolving 0.01 mole (3.37 g) of Co(SAL)$_2$·2H_2O in 100 ml of absolute ethanol was added under N_2 in one addition 0.01 mole (1.03 g) of DIEN dissolved in 25 ml of absolute ethanol. A dark red precipitate formed immediately but after refluxing for some time the reaction mixture turned to a tan color. After refluxing for 2½ hrs. the flask was cooled to room temperature while being flushed with nitrogen. The contents were filtered in an inert atmosphere, dired *in vacuo* at room temperature for 12 hrs. and stored under nitrogen.

Preparation of Co(5–BrSALDIEN)·H_2O 5–BrSAL-(0.01 mole, 4.02 g) was suspended in 75 ml of absolute ethanol. To this suspension was added dropwise a solution formed by dissolving .01 mole (1.03 g) of DIEN in 25 ml of absolute ethanol. To this yellow solution was added another solution prepared by dissolving 0.02 mole (1.12 g) of KOH in 10 ml of H_2O. The reaction mixture was warmed for ½ hr. while being flushed with nitrogen. Next a deoxygenated solution prepared by dissolving 0.01 mole (2.49 g) of Co($C_2H_3O_2$)$_2$·4H_2O in 25 ml of methanol was added dropwise to this mixture which immediately darkened and later turned lighter as a tan precipitate formed in the flask. Warming was continued for another 1½ hrs. after which the compound was isolated and dried as previously described.

Preparation of Co(5-ClSALDIEN)·H_2O, Co(5–NO_2SALDIEN) and Co(3,5-diClSALDIEN). These compounds were prepared following the procedure employed for Co(5–BrSALDIEN)·H_2O with the modification that 5–ClSAL, 5–NO_2SAL and 3,5-diClSAL were substituted for 5–BrSAL.

Preparation of Co(5–CH_3OSALDIEN). A yellow suspension was prepared by adding .01 mole (3.97 gm) of Co(5–CH_3OSAL)$_2$·2H_2O to 75 ml of tert-butanol. To this refluxing suspension under N_2 was added in one addition a solution prepared by dissolving .01 mole (1.03 g) of DIEN in 20 ml of tert-butanol. After addition of the DIEN solution, a precipitate which appeared to be dark red formed in the reaction flask. Refluxing was continued for 2½ hrs. after which the mixture was cooled to room temperature and filtered under nitrogen yielding a yellow-tan product which was then washed with deoxygenated hexane. The compound was dried *in vacuo* for 12 hrs. and stored in an inert atmosphere box.

Preparation of Co(3–CH_3OSALDIEN). A suspension was prepared by adding 0.02 mole (7.94 g) of Co(3–CH_3OSAL)$_2$·2H_2O to 250 ml of 2-propanol. To this refluxing suspension under N_2 was added dropwise a solution prepared by dissolving 0.02 mole (2.06 g) of DIEN in 40 ml of 2-propanol. Refluxing was continued for 1½ hrs. and during this time a dark-red precipitate formed. The mixture was then cooled to room temperature and filtered under N_2. The material was washed with deoxygenated 2-propanol and dried *in vacuo* for 12 hrs.

Physical Measurements Infrared spectra was obtained on Nujol mulls using a Beckman 20–AX recording spectrophotometer over the region 4000–300 cm^{-1}. Magnetic susceptibility data were obtained by the Faraday method at room temperature at several different magnetic fields. Elemental analyses were performed using a Perkin-Elmer Model 240 C, H, and N analyzer. Mass spectra were obtained using a Hitachi Perkin Elmer double focussing mass spectrometer. Each sample was placed on a solid inlet probe and maintained at an appropriate temperature below the point of decomposition. Visible-near infrared spectra in the solid state were obtained on a Cary 14 recording spectrophotometer. Oxygen uptake measurements were made by using a "Warburg-type" gas apparatus designed and made in the Chemistry Department. Thermogravimetric analyses were performed on a Tracor TGA-5 system.

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RESULTS AND DISCUSSION

Cobalt(II) complexes of seven potentially pentadentate ligands with a donor set O_2N_3 have been synthesized. These compounds, all of which have been prepared at least three times, are listed in Table I along with appropriate analytical data. Of the seven complexes prepared, three were obtained as hydrates. The ratio of H_2O to cobalt complex was also confirmed by thermogravimetric analyses. The infrared spectra of these complexes were prepared in a dry atmosphere and each showed a broad absorption band in the 3300–3400 cm^{-1} region. The four complexes which are postulated to be anhydrous showed no O–H stretching vibrational mode in the infrared spectra. These compounds, however, were very hygroscopic and after being exposed to the laboratory atmosphere for only a few minutes showed a broad absorption in the 3250–3400 cm^{-1} region indicative of a rapid absorption of moisture. Analytical measurements on all compounds were performed on hydrated samples.

Magnetic moments on some of the compounds are shown in Table I. The complexes are high spin and the effective moments are in the range expected for either weak field five-coordinate or tetrahedral geometries.[10] Octahedral structures produced by coordination of water or association in the solid state are ruled out by electronic spectra which furnishes strong evidence that these compounds have a tetrahedral configuration. Figure 1 illustrates the type of solid state electronic spectra obtained for the hydrated compounds. Anhydrous material gave similar spectra. Table II lists the peak positions for all the complexes studied. These spectra are similar to those exhibited by Co(RSALDAES) complexes in which it is believed that the central sulfur donor is not coordinated.[3] Thus, at first it would seem that the desire for cobalt to be tetrahedral outweighs its tendency to coordinate the secondary nitrogen. Obviously the smaller carbon chain comes into play here since the longer chain RSALDPT ligands have no difficulty in producing a five-coordinate species. However, a recent x-ray structural analysis on Cu(SALDIEN) has revealed that a five-coordinate complex is produced by dimerization.[11] Such dimers are formed without the major steric problems inherent in a monomeric species. Most likely nickel complexes of RSALDIEN also form this type of five-coordinate compound.[12] Mass spectral analyses have precluded the existence of any dimeric material in the cobalt complexes. The reason for the inability of cobalt to dimerize is not immediately obvious, especially when one considers the x-ray investigation of Ni(SALDPT),[13] a compound isomorphous with Co(SALDPT). Both

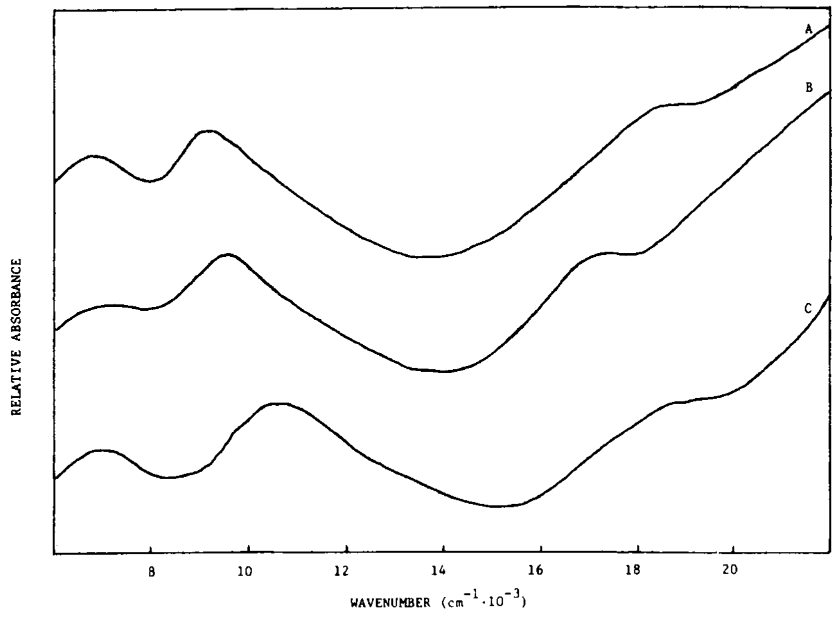

FIGURE 1 Solid state electronic absorption spectra. A, Co(SALDiEN)·$2H_2O$; B, Co(5-ClSALDiEN)·H_2O; C, Co(3-CH_3OSALDiEN)·H_2O.

TABLE I
Analytical data for the cobalt(II) complexes

Hydrated Compound	% C Calcd.	Found	% H Calcd.	Found	% N Calcd.	Found	μ_{eff}(B.M.)
Co(SALDIEN)·$2H_2O$	57.29	57.52	5.30	5.32	11.14	11.23	4.2
Co(5–BrSALDIEN)·H_2O	39.70	39.56	3.49	3.50	7.72	7.71	4.4
Co(5–ClSALDIEN)·H_2O	47.47	47.36	4.17	3.98	9.23	9.31	4.4
Co(5–NO_2SALDIEN)·H_2O	45.37	45.37	3.99	4.21	14.70	14.90	–
Co(3,5–diClSALDIEN)·H_2O	41.22	41.56	3.24	3.16	8.01	7.93	–
Co(3–CH_3OSALDIEN)·H_2O	53.80	53.89	5.60	5.49	9.41	9.36	4.3
Co(5–CH_3OSALDIEN)·H_2O	53.80	53.38	5.60	5.24	–	–	–

Ni(SALDPT) and Cu(SALDIEN) form distorted trigonal bipyramidal structures where the relative positions of the donor atoms are the same even though the latter compound is dimeric.

One clue as to why cobalt may behave differently from nickel came in the form of repeated infrared analyses. Infrared spectra of the cobalt complexes contain two strong absorptions in the region 1590–1610 cm^{-1} which correspond to imine stretching frequencies. When these compounds are exposed to moisture, one of the peaks becomes very weak and is shifted to higher frequency. The other peak showed only slight broadening as a result of this reaction. This suggests that only one of the imine groups is affected by the presence of water. Such a situation could arise if only one is coordinated. This would necessitate the coordination of the secondary amine. Structurally this would result in a highly distorted tetrahedral structure such as that shown in Figure 2. But more importantly it would prevent the type of dimerization observed in Cu(SALDIEN). One could also explain the compounds affinity for water by assuming that molecules of water hydrogen bond to the free imine group. This hydroscopic property was not observed in the Co(RSALDAES) complexes; therefore, we do not believe that a free imine group exists in these compounds. This is also supported by infrared analyses which indicate only one type of imine group exists in these complexes.

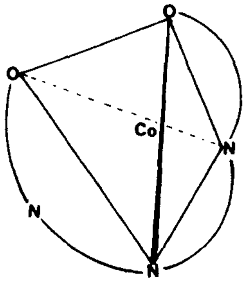

FIGURE 2 Proposed structure for Co(RSALDiEN).

Apparently, the difference between Co(RSALDAES) and Co(RSALDIEN) is that the latter compound has a much stronger central donor.

Another difference between these two types of compounds is that compounds like Co(RSALDAES) are relatively stable and do not react with oxygen in the solid state or in solution. On the other hand, Co(3–CH_3OSALDIEN) and Co(5–CH_3OSALDIEN) react rapidly in the solid state when exposed to oxygen. Furthermore, most of the other derivatives react with dioxygen when suspended in a solvent such as toluene. Table III shows the results of these oxygen uptake measurements. Except for Co(5–BrSALDIEN) which shows a gradual continued uptake, the reaction for the other compounds levels off at an oxygen to cobalt ratio of about 0.5 within experimental error. The compound that goes beyond this point is probably performing some type of catalytic function. Co(5–NO_2SALDIEN) is not included in the Table since it is essentially unreactive. This may be due to either a steric or an electronic effect (i.e. sterically by blocking O_2 access to the cobalt or electronically by removing electron-density from the cobalt making oxidative addition more difficult). This latter explanation seems most likely since it might explain why only the 3–CH_3O and 5–CH_3O derivatives react with oxygen in the solid state.

The 2:1 Co:O_2 ratio suggests a μ-peroxo type dioxygen adduct is formed.[14] The products from these reactions, however, have been very difficult to characterize and no reversible behaviour has been detected. During the course of the reaction, the compounds undergo a color change from yellow-tan to dark brown and these brown compounds persist even when heated at 150°C for 24 hours. Furthermore, the oxygenated products also absorb moisture in the air complicating weight loss experiments. The presence of toluene also hampered efforts in this regard as well as seriously affecting elemental analyses. In solid state reactions where no solvent

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TABLE II
Absorption maxima from the electronic spectra of the cobalt(II) complexes

Hydrated Compound	Band Maxima, cm^{-1} ν_1	ν_2	ν_3	ν_4
$Co(SALDIEN)\cdot 2H_2O$	6800	9100	18,500	25,690
$Co(5-BrSALDIEN)\cdot H_2O$	6880	9390	17,000	24,600
$Co(5-ClSALDIEN)\cdot H_2O$	7250	9530	17,150	25,640
$Co(5-NO_2SALDIEN)\cdot H_2O$	7020	10,250	–	24,200
$Co(5-CH_3OSALDIEN)\cdot H_2O$	6980	10,330	18,250	23,400
$Co(3,5-diClSALDIEN)\cdot H_2O$	7100	10,300	19,050	29,640
$Co(3-CH_3OSALDIEN)\cdot H_2O$	6830	10,650	19,050	26,660

is required, the situation is somewhat simpler. Oxygen uptake still levels off at about the same ratio as when the compound is suspended in toluene. These oxygenated compounds also react with moisture; therefore, elemental analyses were run on hydrated samples. Repeated analyses support the composition $[Co(RSALDIEN)]_2O_2\cdot 4H_2O$ where R = $3-CH_3O$ or $5-CH_3O$. Unlike dioxygen adducts such as $[Co(RSALDPT)]_2O_2\cdot$solvent which are essentially diamagnetic,[8] the solid state dioxygen adducts of Co($3-CH_3O$SALDIEN) and Co($5-CH_3O$SALDIEN) have magnetic moments of about 2.9 B.M. One possible explanation of this anomoly is to consider that the precursors of these compounds are rather unusual tetrahedral complexes. Normally, tetrahedral cobalt(II) complexes are not exceptionally reactive toward oxygen. We cannot suggest the enhanced reactivity is due to coordination of the fifth donor since infrared analyses indicate the presence of a free imine group in the oxygenated species. This is supported by the hydroscopic nature of the compounds.

An explanation to account for these highly paramagnetic dioxygen adducts is not apparent. The ligand could be unique in its electronic and structural features to produce a five-coordinate dioxygen complex. If this were the case, then the splitting of the energy levels in such an environment could conceivably give rise to a ground state with two unpaired electrons assuming a formal cobalt(III). This would explain the high magnetic moment of the dioxygen complexes, but would be unprecendented for compounds of this type. Perhaps this is due to the type of ligands which have been used to date. Schiff bases normally form symmetric ligands. Although RSALDIEN is a symmetric ligand, it apparently does not coordinate in a symmetric fashion. The result is a complex with an unusual set of donor groups and chelate ring sizes. The exceptional irreversibility and paramagnetism may be a feature of this type of compound.

TABLE III
Oxygen uptake data for the cobalt(II) complexes[a]

Compound[b]	η_{O_2}/η_{Co}
$Co(SALDIEN)\cdot 2H_2O$	0.50
$Co(5-ClSALDIEN)\cdot H_2O$	0.41
$Co(5-CH_3OSALDIEN)\cdot H_2O$	0.55
$Co(3-CH_3OSALDIEN)\cdot H_2O$	0.46
$Co(3,5-diClSALDIEN)\cdot H_2O$	0.56
$Co(5-BrSALDIEN)\cdot H_2O$	0.81

[a] P_{O_2} = 800 torr, average of two independent measurements.
[b] Vigorously stirred toluene suspension.

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