of $C_2B_4H_6^{2-}$ are similar in energy (ca. −433.5 eV). However, all of the pentagonal-pyramidal isomers of $C_2B_4H_6^{2-}$ are more stable (apical–basal, −434.4; ortho basal, −436.8; meta basal, −438.1 eV). The results for $C_2B_4H_6^{2-}$ suggest, as in the case of $B_3C_2H_5^{2-}$, that the more open, pyramidal form of the molecule is preferred over any deltahedral structure.[11] Finally, it is interesting to note that Hoffmann's extensive study of the potential surface for $C_5H_5^+$, isoelectronic with $C_2B_3H_5^{2-}$, also indicates a square-pyramidal structure[13] as had been anticipated previously on empirical grounds.[14]

Based on previous studies[1,15] and the results presented here, it is our suspicion that the two-electron reduction of *closo*-carboranes in general opens the deltahedron to the corresponding nido counterpart. However, at least for reduced $C_2B_{10}H_{12}$ molecules, there appears to be some controversy regarding the latter contention vs. the role of subsequent protonation in the opening of the icosahedron upon formation of $C_2B_{10}H_{13}^-$.[16,17]

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Registry No. $C_2B_3H_5^{2-}$, 54844-32-5; $C_2B_4H_6^{2-}$, 54844-33-6.

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Contribution from the Chemistry School,
Melbourne University, Parkville, Victoria, 3052, Australia

Spectrophotometric Study of the Cobalt Chloride–Aluminum Chloride Vapor Complex

P. J. Thistlethwaite* and S. Ciach

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We have recently made a spectrophotometric study of the blue gaseous complex formed by the reaction of solid cobalt chloride with gaseous aluminum chloride. Shortly after submission of our results we discovered that a report of another study of this system was about to be published. Our results are, for the most part, in agreement with those of Papatheodorou[1] but with some significant differences. Also our treatment of the data is somewhat different. We now present an abbreviated account of our work.

Anhydrous $CoCl_2$ was prepared by passing dry gaseous HCl over AR $CoCl_2{\cdot}6H_2O$ at 200°. Pure anhydrous $AlCl_3$ was prepared by distillation from a molten, approximately 6:4 by moles, mixture of AR $AlCl_3$ and AR NaCl. The $AlCl_3$ distilled off ranged in color from almost pure white to pale yellow. Both the $CoCl_2$ and $AlCl_3$ were sealed into previously flamed glass tubes awaiting use.

The absorption cells for the spectrophotometric measurements were constructed of silica and were approximately 7 cm long and 14 mm in diameter, with flat end windows. They were extensively flamed and degassed before being loaded in a N_2 flushed drybox.

The spectrophotometric measurements were done on a Cary 17 spectrophotometer. A special furnace capable of fitting into the cell compartment was constructed. It was designed so as to locate reproducibly in the spectrophotometer when lowered in for a measurement. The furnace was fitted with end-window heaters to ensure that the cell windows always remained slightly hotter than the cell body to prevent condensation.

Four 7-cm cells that had been previously flamed and degassed were each loaded with an excess of anhydrous $CoCl_2$ and varying known amounts of $AlCl_3$. The temperature range of this study was such that the $AlCl_3$ was present entirely as the vapor.[2] Also at the temperature used, the vapor pressure of $CoCl_2$ is virtually zero[2] and thus all measured absorbances were due to the complex. $AlCl_3$ itself has no absorption in the visible region in question. Spectra were scanned between 500 and 700 nm over the temperature range 550–750 K. Care was taken to ensure adequate time for equilibration. At any temperature a number of spectra were run over an extended period to ensure constant absorbance.

The details of the four experiments are given in column 1 of Table I and the results are given as plots of $\log (AT)$ vs. $10^3/T$ in Figure 1. The purpose of the plots in Figure 1 is to improve the data for subsequent treatment (see later). The spectrum of the complex at various temperatures in experiment 4 is shown in Figure 2.

The solid phase was shown to be $CoCl_2$ by X-ray diffraction. At the end of any experiment the cell was cooled in the furnace with the ends cooling somewhat faster. This caused the transport of some blue crystals from the center to the ends of the cell. That this material had been transported was indicated by its highly crystalline nature in contrast to the amorphous appearance of the original $CoCl_2$. Later in the cooling process white $AlCl_3$ was deposited. One cell was opened and the powder pattern for the blue crystals showed only diffraction lines attributable to $CoCl_2$.[3]

The molar absorptivity, ϵ_c, of the complex was determined from the two experiments summarized in Table II. In each experiment a cell was loaded with a known amount of $AlCl_3$ and an amount of $CoCl_2$ sufficiently small so as to ensure that all the $CoCl_2$ was in the vapor phase. The absorbance at the absorption maximum of 633 nm was recorded over the temperature range 650–750 K. At the end of each experiment the cell was opened and washed out with a known volume of dilute acid; the amount of $CoCl_2$ was determined by atomic absorption. The cell volumes were determined by filling with water and weighing. Our values of ϵ_c are considerably lower than the value of approximately 125 $M^{-1}\ cm^{-1}$ found by Papatheodorou[1] and this affects the values of the complex formation constant subsequently calculated. The variation of ϵ_c with temperature might be taken as indicating the existence of more than one complex species. While our other data do not entirely rule out this possibility, we favor the idea of a single complex and believe that most if not all of the variation in ϵ_c is inherent in the complex itself and arises possibly from the fact that the spectrum of the complex is the result of a number of overlapping transitions. A similar decline in ϵ_c with rise

Table I

Expt no. and details	$10^3K/T$	log (AT)	log p_c	p_c/atm	$p''_{Al_2Cl_6}$/atm	log $p''_{Al_2Cl_6}$	K_I
No. 1	1.75	1.88	−1.959	0.011	0.424	−0.373	0.026
$V = 12.5$ cm^3	1.67	2.04	−1.770	0.017	0.439	−0.358	0.038
$p^0_{Al_2Cl_6} = 7.75 \times 10^{-4}T$ atm	1.55	2.29	−1.482	0.033	0.449	−0.348	0.069
$d = 7.3$ cm	1.43	2.54	−1.222	0.060	0.441	−0.356	0.135
No. 2	1.75	2.08	−1.745	0.018	0.534	−0.273	0.034
$V = 12.5$ cm^3	1.67	2.23	−1.569	0.027	0.543	−0.265	0.049
$p^0_{Al_2Cl_6} = 9.67 \times 10^{-4}T$ atm	1.55	2.47	−1.301	0.050	0.555	−0.256	0.090
$d = 7.0$ cm	1.43	2.69	−1.056	0.088	0.542	−0.266	0.162
No. 3	1.75	2.35	−1.482	0.033	0.995	−0.002	0.033
$V = 12.8$ cm^3	1.67	2.50	−1.319	0.048	1.016	0.007	0.048
$p^0_{Al_2Cl_6} = 1.80 \times 10^{-3}T$ atm	1.55	2.73	−1.056	0.088	1.046	0.020	0.085
$d = 7.2$ cm	1.43	2.98	−0.785	0.164	1.029	0.012	0.160
No. 4	1.75	2.53	−1.301	0.050	1.600	0.204	0.031
$V = 12.5$ cm^3	1.67	2.70	−1.108	0.078	1.636	0.214	0.048
$p^0_{Al_2Cl_6} = 2.89 \times 10^{-3}T$ atm	1.55	2.95	−0.833	0.147	1.683	0.226	0.087
$d = 7.1$ cm	1.43	3.21	−0.544	0.286	1.652	0.218	0.173

Table II

Expt no. and details	T/K	Absorbance	ϵ_c/M^{-1} cm^{-1}
No. 1	653	0.285	67.6
$n_{CoCl_2} = 7.48 \times 10^{-6}$ mol	678	0.275	65.2
$V = 12.4$ cm^3	708	0.260	61.6
$p^0_{Al_2Cl_6} = 7.96 \times 10^{-4}T$ atm	738	0.250	59.3
$d = 7.0$ cm			
No. 2	653	0.240	70.7
$n_{CoCl_2} = 6.01 \times 10^{-6}$ mol	678	0.230	67.8
$V = 12.4$ cm^3	708	0.230	67.8
$p^0_{Al_2Cl_6} = 1.14 \times 10^{-3}T$ atm	738	0.220	64.9
$d = 7.0$ cm			

in temperature was found by Papatheodorou.[1] The partial pressure of complex can be calculated from

$$p_c = ART/\epsilon_c d$$

where A is absorbance, T is absolute temperature, ϵ_c is molar absorptivity, and d is optical path length. Now the complex is formed in the reaction

$$n_1\mathrm{CoCl_2(s)} + n_2\mathrm{Al_2Cl_6(g)} \rightarrow \mathrm{Co}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{2n_1+6n_2}\mathrm{(g)} \qquad (1)$$

Thus

$$p_c = K_I p_{Al_2Cl_6}{}^{n_2}$$

and

$$\log p_c = \log (AT) + \log (R/\epsilon_c d) = \log K_I + n_2 \log p_{Al_2Cl_6}$$

Therefore, at a given temperature, a plot of log p_c vs. log $p_{Al_2Cl_6}$ will have a slope of n_2. Values of log (AT) at any temperature can now be read off the lines of best fit of Figure 1, and, using the value of ϵ_c, p_c can be calculated. The results are shown in Table I.

The column headed $p''_{Al_2Cl_6}$ gives the pressure of Al_2Cl_6 corrected for both consumption by complex formation and dissociation to $AlCl_3$. Preliminary calculations had shown that n_2 was approximately 1 and thus this value was used in making the former of the two corrections. The correction for dissociation was made using the relations quoted by Gruen and Oye.[4] Figure 3 shows plots of log p_c vs. log $p''_{Al_2Cl_6}$ at 598 and 698 K. The slopes are 1.08 and 1.15, respectively. We are inclined to take these results as indicating a true value of $n_2 = 1$. The point most likely to be in error is that from experiment 1. The other three points give a slope of very close to unity at both temperatures. The absence of any great difference between the value of n_2 at two temperatures 100 K apart supports the idea of a single complex. The values of n_2 being slightly greater than 1 perhaps provides evidence for a small amount of a complex containing more than one Al_2Cl_6. However, the difference from 1 is probably within experimental error. While it is not strictly possible to rule out polynuclear Co species, the previously studied complexes of this sort[4-6] were

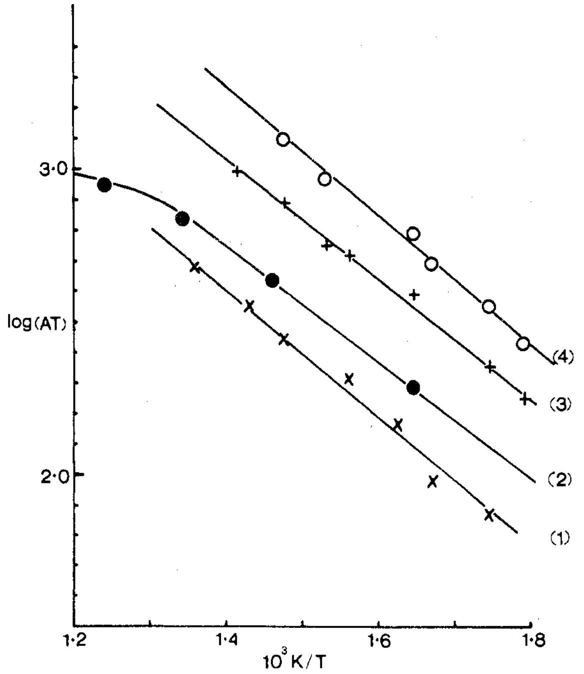

Figure 1. Variation of the absorbance of the complex with pressure of Al_2Cl_6 and with temperature.

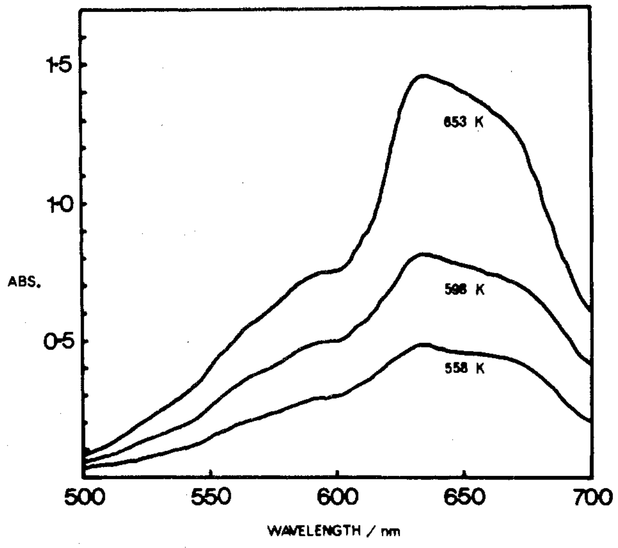

Figure 2. Absorption spectrum of the complex.

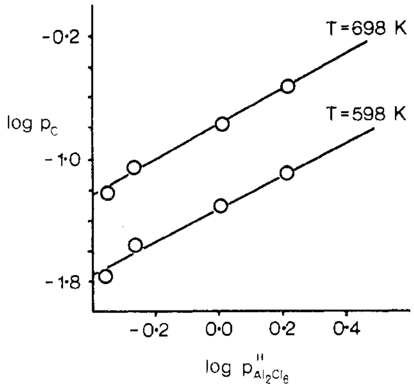

Figure 3. Determination of n_2 at 598 and 698 K.

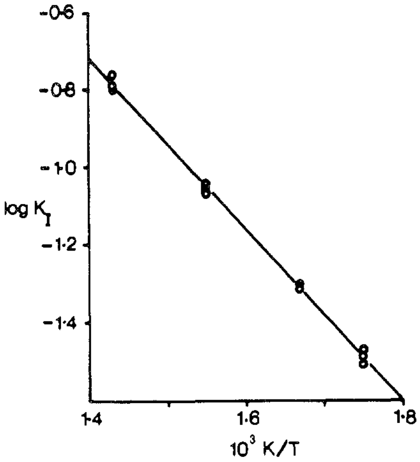

Figure 4. Plot of log K_I vs. $1/T$.

thought to contain only a single transition metal atom. The equilibrium constants of Table I are calculated on the assumption of a $CoAl_2Cl_8$ complex. A second-law deduction of the enthalpy and entropy of equilibrium I is shown in Figure 4. The straight line is the result of a least-squares treatment of the 12 data points of experiments 2–4 (column 8, Table I). Over the temperature range considered ΔH was found to be 42.0 ± 0.7 kJ mol^{-1}. This value is in very close agreement with the value reported in ref 1. Our values of K_I are somewhat higher than in ref 1 due to the difference in the ϵ_c value found. When the value of K_I at 645 K obtained from the least-squares treatment of Figure 4 is combined with the ΔH, a value of 45.0 J K^{-1} mol^{-1} is found for ΔS.

The spectra of Co ions in melts containing $AlCl_3$ have been very fully discussed by Oye and Gruen.[7] Our spectrum for the gaseous complex $CoAl_2Cl_8$ is very similar, both with regard to structure and value of ϵ_c, to that reported by Oye and Gruen for Co ions in an octahedral environment of chlorides. It seems likely that the structure of $CoAl_2Cl_8$ is very similar to that proposed by Papatheodorou[6] for $Ni_2Al_2Cl_8$, i.e., a $CoCl_6$ octahedron, possibly somewhat distorted, sharing faces with two tetrachloroaluminates.

Registry No. $CoCl_2$, 7646-79-9; Al_2Cl_6, 13845-12-0; $CoAl_2Cl_8$, 54822-92-3.

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Contribution from the Research School of Chemistry,
Australian National University, Canberra, A.C.T. 2600,
Australia, and the Department of Inorganic Chemistry,
University of Melbourne, Parkville, Victoria 3052, Australia

Influence of Oxygen and Sulfur Donor Atoms on the Electrochemistry of Transition Metal Tris Chelates

A. M. Bond, R. L. Martin,* and A. F. Masters

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Following the original synthesis of group 8 divalent metal dithioacetylacetonato ($C_5H_7S_2^-$ = SacSac) complexes,[1] the range of complexes of dithio-β-diketonato ligands has been extended to include the electron configurations[2–7] d^3, d^5, d^6, d^7, d^8, and d^{10}. These and the cogeneric acetylacetonato compounds provide an unusual opportunity to compare directly the relative effects of oxygen and sulfur in electron-transfer processes.

Replacement of oxygen by sulfur usually results in spin pairing of metal 3d electrons and a tendency to suppress oligomer formation by complexes with coordinately unsaturated metal centers.[1,4,8–11] Although empirical molecular orbital calculations and electronic spectral assignments have been attempted for dithioacetylacetonato complexes,[12] intense charge-transfer bands obscure most of the visible region precluding comparisons with the d–d transitions of the corresponding acetylacetonato complexes.[13]

Electrochemical studies have been reported for all of the SacSac[2,14–16] complexes. Most of them, in common with metal complexes of other bidentate sulfur ligands,[17–19] undergo one or more reversible one-electron reductions. Donor atom effects in the series $[M–O_4]$,[20] $[M–O_2S_2]$,[21,22] and $[M–S_4]$,[17,18] where the ligands are of the pyrocatechol type, have been investigated by voltammetry, in an endeavor to establish whether the electron-transfer series $[M–O_4]^z$, $[M–O_2S_2]^z$ ($z = 2+ \rightarrow 2-$), similar to that of the 1,2-dithiolenes, occurs. Such studies have been restricted to bis-chelated complexes and have often been beset by problems of nonreversibility and low chemical stability of the oxygen-substituted systems. Whether the lack of reversibility is a function of the structure of the oxygen chelates or simply the inability of oxygen to facilitate fast electron-transfer steps[23] is unknown.

In the present note, the redox properties of a selection of acetylacetonates and dithioacetylacetonates of the transition metals Cr(III), Mn(III), Fe(III), and Co(III) are compared in an attempt to evaluate the kinetic and thermodynamic consequences of substituting oxygen by sulfur in a series of closely related complexes.

Experimental Section

All compounds have been prepared by standard methods[24] and analyzed satisfactorily. Electrochemical experimental details were as reported previously,[14,15] the approximate anodic and cathodic limits being +0.75 and −2.25 V at a DME and +1.5 and −1.3 V at a platinum electrode. The reversibility or otherwise of dc polarograms was established by conventional methods.[25,26] Equations used to evaluate various parameters are given below. Diffusion coefficients, D, were obtained from the equation[25]

$$i_d = 0.732nFCD^{1/2}m^{2/3}t^{1/6} \qquad (1)$$

Cyclic voltammetric results were analyzed via the procedures of Nicholson et al.[26–28]

The reversibility of the ac response has been tested as suggested previously.[29–31] Plots of the ac peak current, $[I(\omega t)]_p$, vs. the square root of the frequency, $f^{1/2}$, were used to investigate the ac electrode

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* To whom correspondence should be addressed at Australian National University.