

sequence S < Se, the difference in K_1 values corresponding approximately to 1.3 kcal/mol in ΔG° . However, no quantitative data are available in the literature concerning the relative affinities of chalcogenide complexes for low-valent transition-metal complexes, although indirect evidence exists that the stability increases in the sequence S < Se < Te (especially with regard to the M-CO bond order deduced from the ν_{CO} 's²⁸ or the loss of carbonyl groups in mass spectral measurements⁴¹). Here, we present the first consistent set of data (solid-state parameters, solution IR studies, and kinetic and thermodynamic measurements) all pointing to an *energetically small* but definite tendency to a larger affinity of both manganese(I) and rhenium(I) for the heavier chalcogen donor.

Our measurements in chloroform solution for the ligand exchange reactions (18) and (19) show that the complex with the heavier chalcogen is favored in the case of rhenium(I). Moreover, the complexes with the heavier chalcogen are more stable with respect to the ligand displacement reaction for tetrahydrofuran. The equilibrium constants of Table X concerning this displacement show that the difference in ΔG° from S to Se is substantially identical with that between selenium and tellurium and amounts to about 2 kcal/mol.

Since the title systems contain neutral chalcogen ligands, solution studies may be carried out in solvents of low polarity and do not require ionic strength adjustments. However, the well-anticipated disadvantage is represented by the fact that our systems contain the two four- and five-member cycles M_2Br_2 and $\text{M}_2\text{E}_2\text{X}$, respectively, with possible consequent ring strains. It is to be noted that the so-called "folding angle" (see Table VI) has its lowest value at tellurium with values of 10.7° (Mn) and 13.2° (Re), which can be taken, to a first approx-

imation, to suggest that the strain is the lowest at tellurium. The release of strain along the sequence S > Se > Te may therefore be at least partly responsible for the observed increased stabilities in the same sequence. However, it will be noted that in the rhenium system the change of folding angle from sulfur (33.0°) to selenium (31.0°) is small and yet the increase of stability is observable.

These results can be used to support the following two propositions. First, the differences in ΔG° values are so small that small changes in bond strengths within the whole framework of a set of chalcogen molecules may change the order of relative tendencies of stability. Second, it is necessary to collect additional data on other related compounds in order to obtain a generalized stability rule. We are planning to extend this study to other chalcogen systems and also to donor atoms of group 5.

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Registry No. I, 85098-02-8; II, 85098-03-9; $\text{Mn}_2\text{I}_2(\text{CO})_6\text{Te}_2\text{Ph}_2$, 85098-04-0; $\text{Re}_2\text{Br}_2(\text{CO})_6\text{S}_2\text{Ph}_2$, 63782-54-7; $\text{Re}_2\text{Br}_2(\text{CO})_6\text{Se}_2\text{Ph}_2$, 72177-50-5; $\text{Re}_2\text{Br}_2(\text{CO})_6\text{Te}_2\text{Ph}_2$, 77805-60-8; $\text{MnBr}(\text{CO})_5$, 14516-54-2; $\text{Mn}_2\text{Br}_2(\text{CO})_8$, 15444-73-2; $\text{MnI}(\text{CO})_5$, 14879-42-6; $\text{Mn}_2\text{I}_2(\text{CO})_8$, 16973-20-9; $\text{MnBr}(\text{CO})_3(\text{thf})_2$, 85165-15-7; $[\text{MnBr}_2(\text{CO})_3(\text{thf})]^-$, 85098-05-1; $[\text{ReBr}_2(\text{CO})_3(\text{thf})]^-$, 85098-06-2; $[\text{ReI}_2(\text{CO})_3(\text{thf})]^-$, 85098-07-3; $[\text{ReBr}_3(\text{CO})_3]^{2-}$, 85098-08-4; $[\text{ReI}_3(\text{CO})_3]^{2-}$, 44863-75-4; CO, 630-08-0; thf, 109-99-9.

Supplementary Material Available: Tables of thermal parameters, selected least-squares planes, interatomic distances and angles, and observed and calculated structure factors for $\text{Mn}_2\text{Br}_2(\text{CO})_6\text{Se}_2\text{Ph}_2$ and $\text{Mn}_2\text{Br}_2(\text{CO})_6\text{Te}_2\text{Ph}_2$, tables of final fractional coordinates and refinement parameters for $\text{Mn}_2\text{Br}_2(\text{CO})_6\text{Te}_2\text{Ph}_2$, and a figure showing the molecular structure of $\text{Mn}_2\text{Br}_2(\text{CO})_6\text{Te}_2\text{Ph}_2$ (28 pages). Ordering information is given on any current masthead page.

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EPR and Electrochemical Studies of Remote Ring Substituent Effects in the Coordination of Dioxygen to (Thio iminato)- and (Keto iminato)cobalt(II) Pyridine Complexes

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Isotropic solution and anisotropic frozen-glass EPR spectra have been recorded for monomeric dioxygen adducts of $\text{Co}(\text{X-benacen})\cdot\text{py}$ and $\text{Co}(\text{X-bensacen})\cdot\text{py}$ species, where the ligands are N,N' -ethylenebis(X-benzoylacetone imine) and N,N' -ethylenebis(X-benzoylthioacetone imine), respectively, and X = meta or para Cl, Br, CH_3 , CH_3O , and H phenyl ring substituents. EPR parameters for both the five-coordinate mono(pyridine) precursors and the six-coordinate dioxygen adducts have been determined. Differences and trends observed for the g values and hyperfine coupling constants have been analyzed in terms of increased covalency in the Co-S bonds indicative of some π -back-bonding. Substituent effects were too small to be observed with EPR methods; however, half-wave potentials obtained on the five-coordinate precursors in dry py/0.1 M TEAP solutions under N_2 do show typical dependence on Hammett σ parameters. The presence of sulfur stabilizes the cobalt ion in lower oxidation states, which correlates with lower thermodynamic stability of these dioxygen adducts. Oxidation of Co(II) to Co(III) occurs at slightly more positive potentials for the para series of complexes, which may indicate some π -resonance effects.

Introduction

Numerous studies on tetradentate Schiff base cobalt(II) oxygen carriers have shown that dioxygen affinity is a function of the amount of electron density at the metal center.¹ This

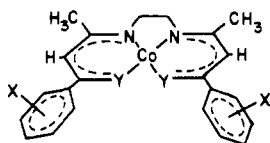
density is affected by the size, charge, donor sets and substituents of the ligands, and whether the ligands are coordinated in the "equatorial" plane of the metal ion or are situated in the "axial" site trans to the dioxygen moiety. Basolo and co-workers² have concluded that the $\text{Co(II)} \rightarrow \text{Co(III)}$ oxi-

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dation potential of the cobalt(II) precursors provides the best measure of total electron density on the metal ion. As long as the axially coordinated Lewis base does not change, a linear correlation of $E_{1/2}$ vs. $\log K_{O_2}$ values is observed for a large number of Co(II) Schiff base² and porphyrin^{3,4} complexes. Oxygen adducts with the greatest thermodynamic stabilities generally result when the in-plane bonding derives from multidentate or macrocyclic ligands with strong σ -donors and electron-donating chelate ring substituents, and the axial interactions involve strong Lewis bases capable of π -bonding.^{5,6} The dioxygen complexes are most conveniently formulated as $Co^{III} \cdot O_2^-$ species, although the degree of electron transfer from Co(II) to O_2 varies with the localized metal ion bonding environment.⁷

For the past several years, we have been studying the oxygenation of ring-substituted (benzoylacetone iminato)cobalt(II), Co(Xbenacen), and (benzoylthioacetone iminato)cobalt(II), Co(Xbensacen), complexes (structure I).⁸ Our thermodynamic studies on oxygenation of the para-X-substituted systems have been reported.⁹ A most interesting discovery was that the type of para substituent on the phenyl ring in the thio imine (bensacen) complexes played a much more important role in stabilizing or destabilizing the oxygen adducts than in the analogous keto imine (benacen) systems. Furthermore, the stability trends observed (Cl > Br > CH₃ ≥ CH₃O >> H) could best be explained by postulating that π -resonance effects dominated σ -bonding interactions.



I

X, para or meta phenyl substituent	Y = O, keto iminato complexes	Y = S, thio iminato complexes
H	Co(benacen)	Co(bensacen)
CH ₃	Co(CH ₃ benacen)	Co(CH ₃ bensacen)
CH ₃ O	Co(CH ₃ Obenacen)	Co(CH ₃ Obensacen)
Br	Co(Br(benacen))	Co(Br(bensacen))
Cl	Co(Cl(benacen))	Co(Cl(bensacen))

In order to further clarify the role of sulfur in these systems and to see whether we could obtain additional evidence for π -bonding between the in-plane sulfur atoms and Co(II) ion, we have undertaken and completed three investigations: (1) synthesis of the corresponding meta-substituted benacen and bensacen complexes, (2) low-temperature EPR studies on all the oxygen adducts and their five-coordinate pyridine adduct precursors, and (3) inert-atmosphere electrochemical studies on the parent complexes in neat pyridine. We reasoned that π interactions should be of lesser importance in the meta systems and that EPR and cyclic voltammetry measurements would enable us to probe any substituent-related electron density differences that might account for the unusual stability trends that we had observed earlier. Results obtained from

each of these investigations are reported herein.¹⁰⁻¹²

Experimental Section

Materials. Analytical reagent grade toluene (Mallinckrodt) was refluxed over CaH₂ for 1 h and distilled under dry nitrogen before use. Spectral-quality dichloromethane (MCB) was refluxed over P₂O₁₀ for several hours prior to distillation under dry nitrogen. Spectral-quality pyridine (MCB) for the EPR studies was stored over KOH pellets for 12 h and then refluxed for 2 h prior to distillation under dry nitrogen. Pyridine for the redox studies was distilled in glass grade (Burdick and Jackson). It was used without further purification. Tetraethylammonium perchlorate (TEAP) (Eastman Kodak) was recrystallized 3 times from water and dried at 60 °C in vacuo prior to use. All other chemicals used were reagent grade or equivalent.

Cobalt(II) Complexes. The series of Co(*p*-Xbenacen) and Co(*p*-Xbensacen) complexes were prepared by our published procedures.⁸ The corresponding meta-X-substituted ligands and complexes were prepared in a similar manner starting from the required meta-X-substituted acetophenones. All complexes used in the EPR and redox studies gave satisfactory C, H, N analyses. Infrared and visible spectral and magnetic susceptibility data on the new meta complexes agreed with the values reported for their para analogues. Since all of the solid complexes are to some degree air sensitive, they were synthesized on a Schlenk line under dry N₂. Samples used in the EPR and CV studies were prepared and handled in a glovebox to preclude contamination by oxygen.

Physical Measurements. EPR spectra were obtained on a Varian E-104A Century Line EPR spectrometer with a 4-in. magnet. A quartz, liquid-N₂ insert dewar was used for frozen-glass measurements. Low-temperature solution spectra were obtained with the Varian variable-temperature accessory. All spectra were recorded in the X band at a frequency of approximately 9.1 GHz. The magnetic field was calibrated before and after each series of measurements by using a Hewlett-Packard HX532B frequency meter and two standards, DPPH (Aldrich) and VO(acac)₂. Calculated *g* values were within ±0.001 of literature values. Samples 10⁻² M in complex and 5–10% by volume in pyridine were prepared in the glovebox with 2:1 v/v toluene/dichloromethane as solvent. Capped samples were frozen in liquid N₂ immediately upon their removal from the box. Spectra were obtained under four sets of conditions: (1) a frozen-glass spectrum of the complex in the presence of pyridine (77 K), (2) an isotropic solution spectrum of the complex in the presence of pyridine (215 K), (3) an isotropic solution spectrum of the complex in the presence of pyridine plus oxygen (215 K), and (4) a frozen-glass spectrum of the complex in the presence of pyridine plus oxygen (77 K). The spectra obtained were typical of those reported for other monomeric dioxygen adducts.¹

Electrochemical measurements were made with a PAR Model 173 potentiostat/galvanostat equipped with a PAR 179 digital coulometer, PAR Model 178 electrometer probe, and PAR 175 universal programmer. The cyclic voltammograms were recorded on a Model 2000 X-Y Houston Omnigraphic recorder. A specially constructed vacuum electrochemical cell equipped with a loading device for air-sensitive compounds was employed¹³ so that samples could be manipulated in a glovebox. The cell consists of a Pt or glassy-carbon (GC) disk working electrode, Pt-wire auxiliary electrode, and Ag-wire quasi-reference electrode. For coulometric experiments, a Pt-gauze electrode was employed. The Pt and GC disk electrodes were polished with alumina prior to use. All voltammograms were obtained in dry pyridine/0.1 M TEAP solutions under N₂. In order to avoid errors associated with liquid-junction potential, ferrocene was used as an internal standard.¹⁴ In addition, by use of ferrocene, problems

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Table I. Selected EPR Parameters^a for Co(Xbenacen) and Co(Xbensacen) Reaction Products

parameter ^{b,c}	py adducts		O ₂ adducts	
	keto	thio	keto	thio
g_x^d	2.438 ^e	2.437 ^e		
g_y^d	2.236	2.185		
g_z	2.011	2.006		
$ A_x^{Co} ^d$	51.1–55.3 ^f	26–31 ^g		
$ A_z^{Co} $	91.7 ^f	69.8 ^f		
$ A_z^{N} $	15.0	15.0		
g_{iso}			2.026	2.026
$ A_{iso} $			12.3	12.3
g_{\perp}^h			1.997	1.997
g_{\parallel}			2.084	2.082
$ A_{\perp}^{Co} ^i$			9.5	8.4
$ A_{\parallel}^{Co} $			18.1 ^f	20.6 ^f

^a No meaningful A_y^{Co} values could be determined in the absence of computer simulation; hence, none are reported. ^b All single values listed are averages of values obtained within each X-substituted series; g values in gauss, A values in $\text{cm}^{-1} \times 10^{-4}$. ^c Errors = 1 in final digits unless indicated differently. ^d The x and y directions are arbitrarily assigned but lie in the average Schiff base plane. ^e Error is ± 0.005 . ^f Error is ± 0.5 . ^g Error is ± 2 . ^h Calculated from the equation $g_{\perp} = (3g_{iso} - g_{\parallel})/2$. ⁱ Calculated from the equation $A_{\perp}^{Co} = (3A_{iso}^{Co} - A_{\parallel})/2$.

associated with under- or overcompensated solution resistance were avoided by adjusting the iR compensation so that Fc^+/Fc cyclic voltammograms showed a peak separation of ~ 60 mV. Half-wave potentials were calculated by using the formula $E_{1/2} = (E_{pa} + E_{pc})/2$ for reversible electron transfer. Potential values reported herein are an average of three independent measurements and are believed to be accurate to within 0.003 V. The ratio of the anodic to the cathodic peak current was determined as suggested by Adams.¹⁵

Since the investigated compounds are particularly sensitive to oxygen in solution, special precautions were taken so that all oxygen was removed from the pyridine prior to the addition of each complex. It is difficult to remove minute traces of oxygen from pyridine simply by bubbling nitrogen through the solution or by classic freeze-pump-thaw procedures. We have found that degassing pyridine by a procedure similar to that described by Battino gave very satisfactory results.¹⁶ The presence of dissolved oxygen in pyridine can be detected conveniently with cyclic voltammetry by the appearance of a reduction wave at -0.80 V corresponding to the one-electron formation of superoxide ion. The wave is well developed and is electrochemically reversible on Pt or GC electrodes. After the cell was degassed by the Battino method, no oxygen was detected even after 24 h.

Results and Discussion

EPR Studies. Measured and calculated g values, hyperfine splitting constants, and hyperfine coupling constants for the five-coordinate mono(pyridine) and six-coordinate oxygen adducts are listed in Supplementary Tables I–IV. The values of g_x , g_y , and g_z have been assigned on the basis of observed superhyperfine splittings and additional spectral measurements of the complexes in an oriented nematic liquid crystal by using the procedure of Fackler¹⁷ as adapted by Hoffman.¹⁸ EPR parameters for the para and meta systems are virtually indistinguishable. Typical values obtained for the five-coordinate pyridine precursors and six-coordinate oxygen adducts are reported in Table I. Although small differences are evident in A_x^{Co} values for each complex of the Co(Xbenacen)·py and Co(Xbensacen)·py series, no trends as a function of the X

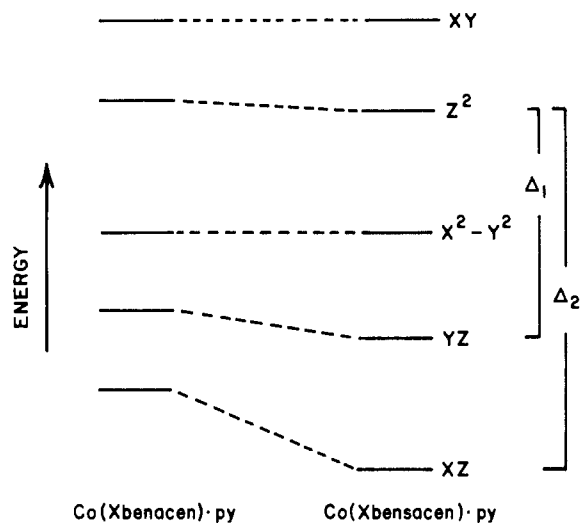


Figure 1. Hypothetical crystal field energy diagrams for Co(Xbenacen)·py and Co(Xbensacen)·py illustrating the effects of π -back-bonding in the sulfur systems. Coordinates used: z axis is perpendicular to the Schiff base plane, x axis bisects the iminato rings.

substituent could be identified since the differences in coupling constants are very close to the error limits of the measurements. Analysis of the data via computer simulation techniques¹⁹ might provide more accurate values of the EPR parameters, but it is probable that any differences related to substituent effects in these systems are too small to be evaluated by EPR methods, since the substituents are far removed from the center of EPR activity. Similar findings have been reported for remote substituent effects in porphyrin²⁰ and carboxaldehyde complexes.²¹

Significant differences are noted when comparisons are made between the EPR parameters determined for the corresponding keto vs. thio systems. In all cases, the presence of S in the tetradentate ligand leads to smaller values of A_z^{Co} and A_x^{Co} for the mono(pyridine) adducts. This can be correlated with a weaker σ -donating effect for the S atoms. After oxygenation, A_{\perp}^{Co} is found to be larger for the sulfur system, which suggests less charge transfer and a formulation of $\text{Co}^{\text{II}}\text{-O}_2$ rather than $\text{Co}^{\text{III}}\text{-O}_2^-$ for the oxygenated species. Indeed, our electrochemical studies have shown (vide infra) that (keto iminato)cobalt(II) is much easier to oxidize than (thio iminato)cobalt(II). These results are reasonable since ligands of the σ -donor- π -acceptor type are known to stabilize metal ions in lower oxidation states. These data support our earlier hypothesis that there is considerable π -back-bonding between the S donors and cobalt(II) ion.⁹

Theoretical studies of Co(benacen)·py² and other (keto iminato)cobalt(II) pyridine adducts^{22–24} have established that the ground state for these complexes is $^2A(z^2)^1$. The ground-state configuration may be written formally as $d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^2 d_{z^2}^1$. The effect of in-plane π -bonding with sulfur on the Co(II) d-orbital energies is illustrated in Figure 1, where the relative energies of the d orbitals are deduced as described by Drago.²⁵ With the assumption of the above ground state, the EPR parameters can be analyzed by the relationships

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$$g_z = 2.0023$$

$$g_x = 2.0023 + \frac{6\zeta}{\Delta_1(E_{z^2} - E_{yz})} = 2.0023 + 6b_1$$

$$g_y = 2.0023 + \frac{6\zeta}{\Delta_2(E_{z^2} - E_{xz})} = 2.0023 + 6b_2$$

where ζ is the spin-orbit coupling constant and E is the relative crystal field energy of the ground and excited states. Substitution of the g values obtained for Co(Xbenacen)·py and Co(Xbensacen)·py into these equations shows that $b_1(\text{thio}) \approx b_1(\text{keto})$ but $b_2(\text{thio}) < b_2(\text{keto})$. This translates into $\Delta_1(\text{thio}) \approx \Delta_1(\text{keto})$ but $\Delta_2(\text{thio}) > \Delta_2(\text{keto})$; i.e., the d_{xz} orbital (and to a lesser extent the d_{yz}) in the thio systems is stabilized with respect to the d_{z^2} orbital; at the same time, the d_{z^2} orbital in the thio systems should be at a somewhat lower energy than in the keto systems because of weaker in-plane σ -bonding. This prediction is confirmed by results of our redox studies that show that the Co(Xbenacen)·py complexes are more easily oxidized than their thio iminato counterparts (see below).

Electrochemical Studies. Cyclic voltammograms of all investigated compounds in anhydrous pyridine are similar in shape and reversibility and exhibit both an oxidation and a reduction wave corresponding formally to Co(II) → Co(III) oxidation and Co(II) → Co(I) reduction processes.

Co(II) → Co(III) Oxidation Process. A comparison of cyclic voltammograms at Pt and GC electrodes for the Co(*p*-Cl(bensacen)) complex can be made from Figure 2. At a Pt electrode (Figure 2b), the electron-transfer process is very slow and CV shows quasi-reversible behavior even at a very slow scan rate (~5 mV/s). The peak potential separations, ΔE_p of ~250–300 mV, are much larger than the expected values of ~60 mV for a fast electron-transfer process. The ratio of anodic and cathodic peak currents was ~1 although the voltammograms lack the characteristic "sharpness" of a reversible electrode process. The waves have much better definition and show the characteristic shape of a relatively faster electron-transfer process when a glassy-carbon electrode is used (Figure 2a). Indeed, at a scan rate of 10 mV/s, the oxidation wave shows Nernstian behavior. With a higher scan rate, the peak separation increases while the ratio of i_{pc}/i_{pa} remains at 1, indicating quasi-reversible behavior. Coulometric experiments performed on some of the compounds confirmed that this wave corresponds to a one-electron oxidation process.

$E_{1/2}$ and ΔE_p values for all complexes obtained at selected scan rates with the GC electrode are shown in Table II. The tabulated data illustrate in a most striking manner that the bensacen ligands stabilize the cobalt ion in its lower oxidation states, since the Co(Xbensacen) complexes are oxidized at ~250 mV more positive potential than the corresponding benacen complexes. The lesser thermodynamic stability, which we previously reported for all Co(*p*-Xbensacen)·py·O₂ adducts, correlates with the difficulty in oxidizing Co(II) to Co(III) in these systems.⁹

Co(II) → Co(I) Reduction Process. A well-developed reduction wave can be observed at about -2.1 V for the keto iminato complexes and at approximately -1.8 V (vs. Fc⁺/Fc) for the thio iminato complexes. This reduction process is electrochemically reversible, since the separation between the peak potentials is ~60 mV for all complexes, and does not increase with increased scan rates up to 200 mV/s. Unlike the Co(II) → Co(III) oxidation process, the Co(II) → Co(I) electron-transfer process is relatively fast on both GC and Pt electrodes. The ratio of anodic to cathodic peak currents is equal to 1 for all complexes of the thio iminato series at both slow (5 mV/s) and fast (200 mV/s) scan rates. For the Co(Xbenacen) complexes, excluding the Co(Br(benacen)) derivatives, this ratio is slightly less than 1 at 5 mV/s, but it

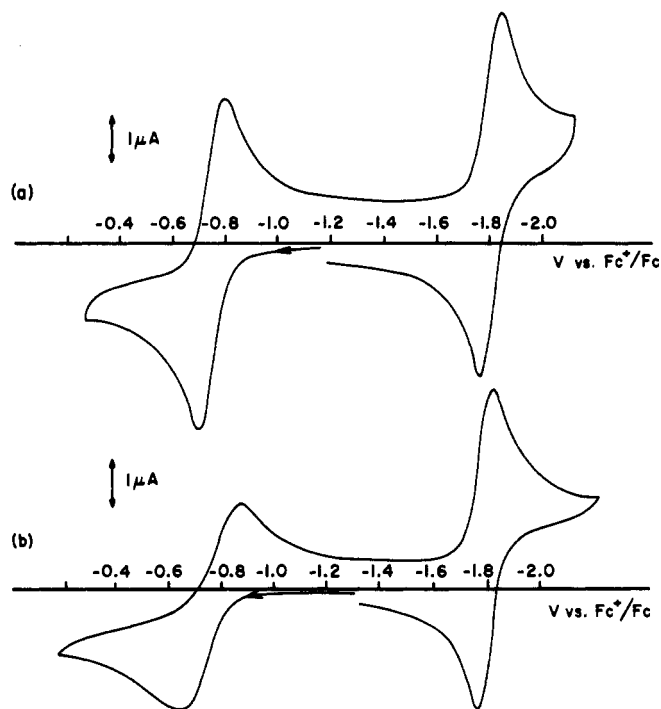


Figure 2. Cyclic voltammograms of Co(*p*-Cl(bensacen)) at (a) a glassy carbon electrode and (b) a Pt electrode in 0.1 M TEAP/pyridine (sweep rate = 10 mV/s).

Table II. Half-wave Potentials^a for Co(Xbenacen)·py and Co(Xbensacen)·py Complexes

complex·py	Co(II) → Co(III)			Co(II) → Co(I)			
	$E_{1/2}$, mV ^b	E_p	i_{pa}/i_{pc}	5 mV/s	10 mV/s	i_{pa}/i_{pc}	
				$E_{1/2}$, mV ^b	E_p	10	50
				mV/s	mV/s		
Co(benacen)	-1035	60	1.00	-2117	60	0.98	1.00
Co(<i>p</i> -CH ₃ Obenacen)	-1048	60	1.00	-2154	60	0.85	1.00
Co(<i>p</i> -CH ₃ benacen)	-1037	63	1.00	-2133	60	0.93	1.00
Co(<i>p</i> -Br(benacen))	-1019	62	1.00	-2088	60	<i>c</i>	0.3 ^d
Co(<i>p</i> -Cl(benacen))	-989	60	1.00	-2071	60	1.00	1.00
Co(<i>m</i> -CH ₃ benacen)	-1033	60	1.00	-2126	60	0.98	1.00
Co(<i>m</i> -CH ₃ Obenacen)	-1028	60	1.00	-2100	60	1.00	1.00
Co(<i>m</i> -Cl(benacen))	-991	60	1.00	-2055	60	1.00	1.00
Co(<i>m</i> -Br(benacen))	-990	64	1.00	-2053	60	0.74	0.83
Co(bensacen)	-779	66	1.00	-1845	60	1.00	1.00
Co(<i>p</i> -CH ₃ Obensacen)	-798	62	1.00	-1880	60	1.00	1.00
Co(<i>p</i> -CH ₃ bensacen)	-785	67	1.00	-1865	60	1.00	1.00
Co(<i>p</i> -Cl(bensacen))	-756	61	0.99	-1811	60	1.00	1.00
Co(<i>p</i> -Br(bensacen))	-755	62	0.98	-1798	60	1.00	1.00
Co(<i>m</i> -CH ₃ bensacen)	-782	60	0.98	-1860	60	1.00	1.00
Co(<i>m</i> -CH ₃ Obensacen)	-762	65	1.00	-1828	60	1.00	1.00
Co(<i>m</i> -Br(bensacen))	-750	60	1.00	-1784	60	1.00	1.00
Co(<i>m</i> -Cl(bensacen))	-740	60	1.00	-1785	60	1.00	1.00

^a Measured in 0.1 M TEAP/py at 25 °C vs. Fc⁺/Fc under vacuum.

^b Error is ±3 mV. ^c No anodic peak observed on a reverse scan.

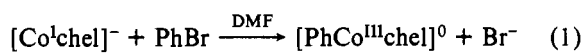
^d 0.61 at 500 mV/s scan rate.

reaches a value of 1 at 50 mV/s. Both meta- and para-bromo derivatives of Co(Br(benacen)) show unexpected behavior. At scan rates of 5 mV/s, a cathodic peak is clearly shown for the reduction of Co(*p*-Br(benacen)), but no reverse peak is observed. At faster scan rates, the reverse peak becomes apparent but the ratio reaches a value of only 0.3. This is a much lower value than observed for other benacen derivatives obtained under the same conditions. Clearly, something unusual is taking place. It has been reported²⁶ that certain Co(I) Schiff

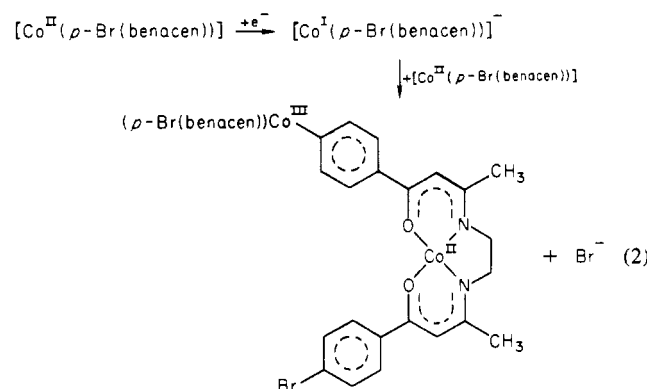
Table III. Correlations of Co(II) → Co(III) and Co(II) → Co(I) $E_{1/2}$ Values with Hammett Constants for Substituted Derivatives of Co(Xbenacen) and Co(Xbensacen)

compd	redox process	reacn const (ρ) (slope)	R	variance
Co(Xbenacen)	Co(II) → Co(III)	0.0446	0.917	0.0004
	Co(II) → Co(I)	0.0754	0.989	0.0011
Co(Xbensacen)	Co(II) → Co(III)	0.0380	0.980	0.0003
	Co(II) → Co(I)	0.0761	0.991	0.0011

base chelates react with phenyl bromide to form organometallic derivatives of Co(III) (eq 1) where the phenyl group is bonded



directly to the cobalt ion. It is possible that in the case of the Co(Br(benacen)) derivatives, electrochemically generated Co(I) species react with nonreduced Co^{II}(Br(benacen)) to form dimers attached through the phenyl group (eq 2). The nu-

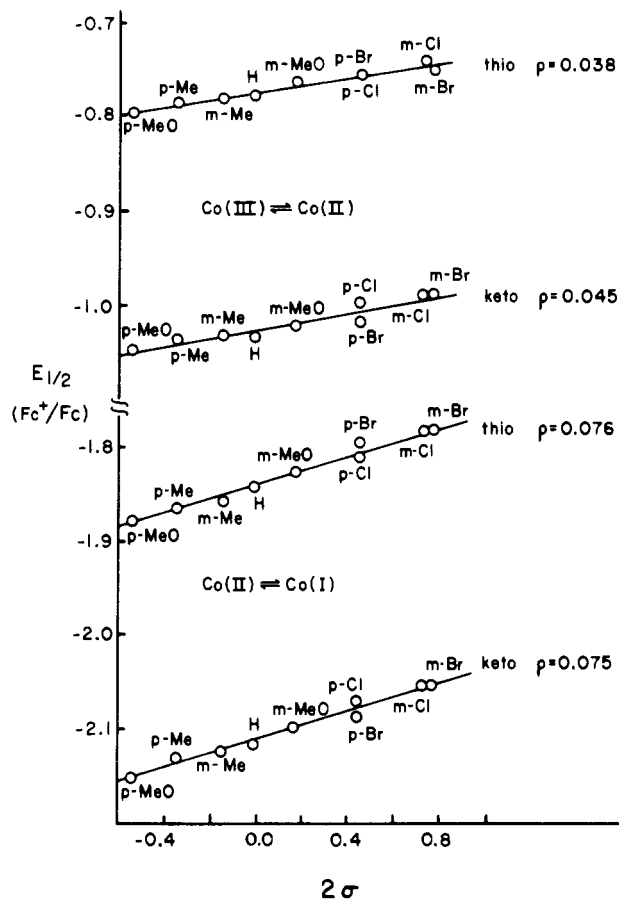


cleophilicity of Co(I) species was observed primarily for Co(*p*-Br(benacen)), to a lesser extent for Co(*m*-Br(benacen)), and not at all for the thio iminato species. This may be due to the larger negative $E_{1/2}$ potential of the keto iminato species.

Linear Hammett Correlations. The results of Table II clearly show that both Co(II) → Co(III) and Co(II) → Co(I) redox processes are sensitive to the nature and position of the remote substituents present on the phenyl groups. In general, electron-withdrawing groups such as Br or Cl produce $E_{1/2}$ values less negative than do electron-donating groups such as CH₃ or CH₃O; i.e., electron-withdrawing groups make reduction of Co(II) to Co(I) easier and oxidation of Co(II) to Co(III) more difficult than do electron-donating groups. The dependence of $E_{1/2}$ values on the electronic properties of the substituent groups was examined by means of the Hammett²⁷ linear free energy relationship, where the relevant Hammett equation is

$$E_{1/2} = 2\sigma\rho$$

because of the presence of two substituents. The reaction constant ρ expresses the susceptibility of the electrode reaction to the total polar effect of the substituents while σ is the polar substituent constant. The correlations are shown in Figure 3, and the magnitudes of the reaction constants and correlation factors obtained via least-squares analysis are given in Table III. Larger values of the reaction constants (steeper but parallel slopes) for the Co(II) ⇌ Co(I) couples compared to those for the Co(III) ⇌ Co(II) couples show that the former redox processes are more sensitive to equatorial ligand effects. Similar results have been reported for Co(II) porphyrin sys-

**Figure 3.** Plot of $E_{1/2}$ of para- and meta-X-substituted benacen and bensacen derivatives vs. the Hammett 2σ parameter.

tems³ and vitamin B₁₂ model complexes;⁴ however, these complexes contained only para substituents. The positive nature of all slopes indicates that the placement of electron-withdrawing substituents on the two benzoyl rings inhibits oxidation of the cobalt ion. Similar results have been reported for Schiff base metal complexes with macrocyclic and noncyclic ligands.^{28,29} It should be noted that the trend in potentials for CH₃ and CH₃O is reversed in the para-X and meta-X series. The para-methoxy substituent facilitates oxidation to Co(III), which is reasonable if it is assumed that both inductive and π -resonance contributions are present. Some π contributions are suggested also by the fact that it is slightly easier to oxidize the para-Cl and -Br derivatives compared to the meta analogues. However, inspection of Figure 3 and the correlation factors reported in Table III show that there is no significant deviation from the linear Hammett relationship, which would be expected if there were a large resonance effect associated with para substitution. This suggests that the influence of the remote ring substituents is essentially inductive regardless of the position of the substituent. The somewhat larger values of the benacen reaction constants, for Co(II) → Co(III) oxidation, indicate that the effective transmission of the electronic influence of the remote substituent is better achieved through the O than through the S atom. The reaction constants for Co(II) → Co(I) reduction are approximately the same.

Because the values obtained for the Co(II) → Co(III) oxidation potentials of the Co(*p*-Xbensacen)·py and Co(*p*-Xbenacen)·py species exhibit rather typical Hammett behavior, they provide no rationale for understanding the unusual

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thermodynamic stabilities of the related oxygen adducts. Recently, we have investigated the thermodynamics of oxygenation of the series of $\text{Co}(m\text{-Xbensen})\text{-py}$ complexes in low-temperature toluene solutions.³⁰ Our preliminary results show that the stability order here again is unusual, i.e., $\text{Br} > \text{Cl} > \text{CH}_3 \geq \text{CH}_3\text{O} > \text{H}$. At present, we are unable to explain these trends. Clearly, π interactions appear to be very small. Thus, solvent effects may be of prime importance. Recent studies have documented the importance of solvent effects on redox reactions of various porphyrins.^{31,32} In our case, solvents used were different for each type of study so no direct comparisons can be made. Other factors to be considered include steric effects related to the large sulfur atoms and/or kinetic stability differences related to σ and π interactions and their effect on the rate of the "on" and "off" oxygenation reactions.

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Registry No. I (X = H, Y = S)-py, 68843-00-5; I (X = *p*-CH₃, Y = S)-py, 68842-96-6; I (X = *p*-CH₃O, Y = S)-py, 68842-97-7; I (X = *p*-Br, Y = S)-py, 68842-98-8; I (X = *p*-Cl, Y = S)-py, 68842-99-9; I (X = H, Y = O)-py, 50723-30-3; I (X = *p*-CH₃, Y = O)-py, 68842-94-4; I (X = *p*-CH₃O, Y = O)-py, 68924-08-3; I (X = *p*-Br, Y = O)-py, 68842-95-5; I (X = *p*-Cl, Y = O)-py, 68850-90-8; I (X = H, Y = S)-py-O₂, 68851-23-0; I (X = *p*-CH₃, Y = S)-py-O₂, 68851-19-4; I (X = *p*-CH₃O, Y = S)-py-O₂, 68851-20-7; I (X = *p*-Br, Y = S)-py-O₂, 68851-21-8; I (X = *p*-Cl, Y = S)-py-O₂, 68851-22-9; I (X = H, Y = O)-py-O₂, 36466-13-4; I (X = *p*-CH₃, Y = O)-py-O₂, 68851-15-0; I (X = *p*-CH₃O, Y = O)-py-O₂, 68851-16-1; I (X = *p*-Br, Y = O)-py-O₂, 68851-17-2; I (X = *p*-Cl, Y = O)-py-O₂, 68851-18-3; I (X = *m*-CH₃, Y = S)-py, 85422-52-2; I (X = *m*-CH₃O, Y = S)-py, 85422-53-3; I (X = *m*-Br, Y = S)-py, 85422-54-4; I (X = *m*-Cl, Y = S)-py, 85422-55-5; I (X = *m*-CH₃, Y = O)-py, 85422-56-6; I (X = *m*-CH₃O, Y = O)-py, 85422-57-7; I (X = *m*-Br, Y = O)-py, 85422-58-8; I (X = Cl, Y = O)-py, 85422-59-9; I (X = *m*-CH₃, Y = S)-py-O₂, 85422-60-2; I (X = *m*-CH₃O, Y = S)-py-O₂, 85422-61-3; I (X = *m*-Br, Y = S)-py-O₂, 85422-62-4; I (X = *m*-Cl, Y = S)-py-O₂, 85422-63-5; I (X = *m*-CH₃, Y = O)-py-O₂, 85422-64-6; I (X = *m*-Br, Y = O)-py-O₂, 85422-65-7; I (X = *m*-Cl, Y = O)-py-O₂, 85422-66-8.

Supplementary Material Available: Listings of measured and calculated EPR parameters for all complexes (4 pages). Ordering information is given on any current masthead page.

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Zintl Anions from the Extraction of Zintl Phases with Non-Amine Solvents: Isolation of $(\text{Me}_4\text{N})_4\text{Sn}_9$, $[\text{K}(\text{HMPA})_2]_4\text{Sn}_9$, and K_4SnTe_4 and Structural Characterization of $(\text{Bu}_4\text{N})_2\text{M}_x$ (M = Te, $x = 5$; M = Se, $x = 6$; M = S, $x = 6$)

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Polyatomic main-group anions like Sn_9^{4-} , Te_5^{2-} , Se_6^{2-} , S_6^{2-} , and SnTe_4^{4-} have been isolated without the use of cryptate ligands. The polychalcogenides $(\text{Bu}_4\text{N})_2\text{M}_x$ (where M = Te, $x = 5$; M = Se, $x = 6$; M = S, $x = 6$; Bu = *n*-C₄H₉) are obtained by the aqueous extraction of binary alkali-metal/main-group alloys in the presence of Bu_4NBr . These polychalcogenides are amorphous and have been structurally characterized by X-ray crystallography. The nonastannide(4-) anion has been isolated both as the tetrakis(tetramethylammonium) compound, $[(\text{CH}_3)_4\text{N}]_4\text{Sn}_9$, and as the HMPA (hexamethylphosphoric triamide) solvate, $[\text{K}(\text{HMPA})_2]_4\text{Sn}_9$. Both compounds are somewhat thermally unstable at 25 °C. The compound K_4SnTe_4 has been isolated by the aqueous extraction of ternary K/Sn/Te alloys.

Although the existence of solution-phase polyatomic main-group anions has been known for over 50 years,¹ they have received very little attention relative to other major classes of clusters (e.g., borane and transition-metal polyhedra). Recently there has been renewed interest in the homo- and heteroatomic main-group polyanions (Zintl anions) derived from the Zintl phases,² which are alloys composed of an alkali or alkaline-earth metal and one or more main-group elements. Numerous examples of polyanions devoid of intercluster metal-metal interactions such as Sn_9^{4-} ,³ Te_5^{2-} ,⁴ Sb_7^{3-} ,⁵ and Bi_4^{2-} ⁶ have been isolated by Corbett and co-workers through the use of cryptate ligands in amine solvents.⁷ Schäfer and co-workers have prepared (by high-temperature methods) and characterized a large number of Zintl phases that contain substantial intercluster interaction. Recent examples include the two structurally different forms of $(\text{Si}_2\text{As}_4)^{6-}$,⁸ in $\text{Ca}_3\text{Si}_2\text{As}_4$ and $\text{Sr}_3\text{Si}_2\text{As}_4$ and the $(\text{AlAs}_3)^{6-}$ anion⁹ in Ca_3AlAs_3 .¹⁰ We would like to report the convenient preparation and charac-

terization of several novel main-group anions, without the use of cryptates or amine solvents. examples include the structurally characterized isomorphous series of polychalcogenides $(\text{Bu}_4\text{N})_2\text{M}_x$ (M = Te, $x = 5$; M = Se, $x = 6$; M = S, $x = 6$), noncryptated nonastannide(4-) anions such as $(\text{Me}_4\text{N})_4\text{Sn}_9$ and $[\text{K}(\text{HMPA})_2]_4\text{Sn}_9$, and anhydrous Zintl phases such as K_4SnTe_4 .

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