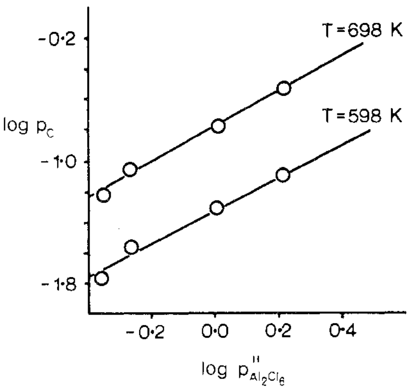

Figure 3. Determination of n_2 at 598 and 698 K.

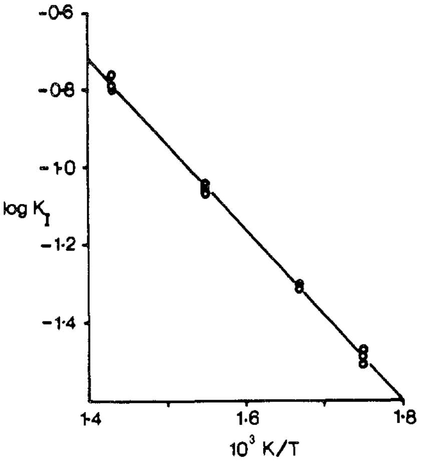

Figure 4. Plot of log K_I vs. $1/T$.

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.

References and Notes

(1) G. N. Papatheodorou, *Z. Anorg. Allg. Chem.*, in press.
(2) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).
(3) American Society for the Testing of Materials, Powder Diffraction File No. 15, 1966, p 381.
(4) H. A. Oye and D. M. Gruen, *J. Am. Chem. Soc.*, **91**, 2229 (1969).
(5) E. W. Dewing, *Metall. Trans.*, **1**, 2169 (1970).
(6) G. N. Papatheodorou, *J. Phys. Chem.*, **77**, 472 (1973).
(7) H. A. Oye and D. M. Gruen, *Inorg. Chem.*, **4**, 1173 (1965).

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

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Received September 19, 1974 AIC40656F

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]

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

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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Table I. Dependence of $E_{1/2}$ on Drop Time

	$E_{1/2}$ at stated drop time, V				
Compd[a]	4.93[b]	1.98[b]	1.0[b]	0.5[b]	0.17[b]
$Mn(acac)_3$	+0.028	+0.027	+0.027	+0.025	+0.024
$Fe(acac)_3$	−0.576	−0.575	−0.578	−0.578	−0.576
$Co(acac)_3$	−0.250	−0.270	−0.293	−0.298	
$Cr(SacSac)_3$	−0.493	−0.493	−0.492	−0.493	−0.492

[a] The merging of the two waves of $Cr(acac)_3$ at long drop times precluded such studies on this compound, as $E_{1/2}$ could be calculated only at short drop times. [b] Drop time (sec).

process over the frequency range $20 \lessapprox f \lessapprox 1100$ Hz. The gradients of these plots also provide a check of the diffusion coefficients for reversible cases. The charge-transfer coefficient, α, was evaluated using the equation[32]

$$[E_{\mathrm{dc}}]_{\mathrm{p}} - E_{1/2}{}^{\mathrm{r}} = \frac{RT}{nF} \ln \left(\frac{1-\alpha}{\alpha} \right) \tag{2}$$

and k_s, the rate constant for the heterogenous charge-transfer, from[32]

$$[I(\omega t)]_{\mathrm{p}} = \frac{n^2F^2AC\Delta E k_{\mathrm{s}}}{2RT} \tag{3}$$

the drop area, A, being calculated via[25]

$$A = 0.85(mt)^{2/3} \tag{4}$$

All graphical analyses were refined by least-squares procedures. Experiments were performed at a controlled temperature of 22°.

Results and Discussion

Chromium. Both $Cr(SacSac)_3$ and $Cr(acac)_3$ exhibit two one-electron reductions at a DME. No oxidation of either compound is observed at mercury or platinum electrodes. The first reduction of $Cr(SacSac)_3$ has been shown[2] to be diffusion controlled and reversible in the dc sense and is affected neither by changes in drop time nor electrode material (Tables I and II). It is also essentially reversible in ac polarography over a wide frequency range. At high frequencies, the slight difference between the ac peak potential, $[E_{\mathrm{dc}}]_{\mathrm{p}}$, and $E_{1/2}{}^{\mathrm{r}}$ yields $\alpha = 0.46$ via eq 2, a value close to 0.5 being consistent with the polarographic behavior of all the present compounds. A value of $\alpha = 0.5$ is assumed in calculations of k_s for compounds where α could not be evaluated. Although a plot of $[I(\omega t)]_{\mathrm{p}}$ vs. $f^{1/2}$ begins to deviate from linearity at very high frequencies (Figure 1), this departure is insufficient to permit the unambiguous calculation of k_s, since small terms due to uncompensated resistance could well explain the slight nonlinearity. However, it is possible to assign a lower limit to k_s (Table III).

The second $Cr(SacSac)_3$ reduction was previously reported[2] to be irreversible and assumed to be associated with product degradation. This postulate is now confirmed. Only in the limit of short controlled drop times (~0.1 sec) are the heights of the two $Cr(SacSac)_3$ waves equal. Cyclic voltammetry at a DME shows the second wave to be more nearly reversible than the corresponding $Cr(acac)_3$ reduction and at a platinum electrode establishes that the first electron-transfer step of

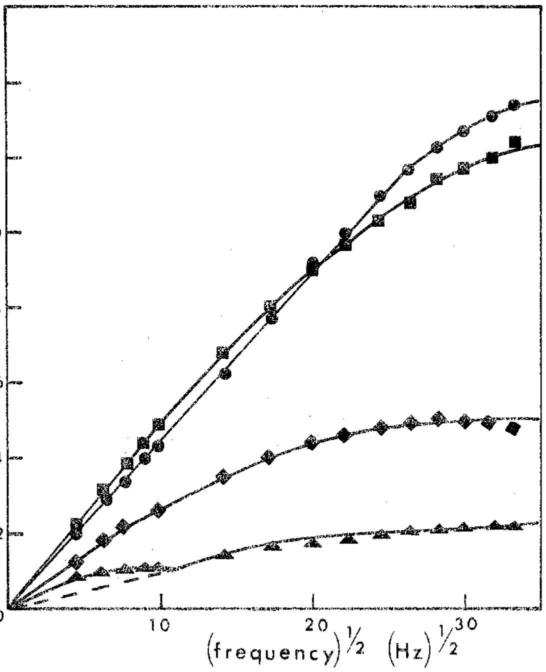


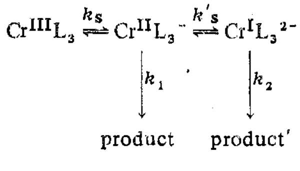
Figure 1. Ac frequency dependence of the first reduction waves of the chelates: ●, $Cr(SacSac)_3$; ■, $Fe(acac)_3$; ◆, $Mn(acac)_3$; ▲, $Cr(acac)_3$.

$Cr(SacSac)_3$ is also very fast at this electrode surface (Table III).

Both $Cr(acac)_3$ reduction waves are extremely drop-time dependent. Only at very short drop times (0.05 sec) are the wave heights approximately equal. Cyclic voltammetry at a DME establishes the chemical nonreversibility of the electrode processes of $Cr(acac)_3$. In ac polarography $[E_{\mathrm{dc}}]_{\mathrm{p}}$ of the first step, although not markedly frequency dependent, is slightly more negative than $E_{1/2}$ at the same drop time. A plot of $[I(\omega t)]_{\mathrm{p}}$ vs. $f^{1/2}$ for the first reduction is nonlinear up to about 100 Hz (influence of chemical reaction). From 100 to 500 Hz, a linear plot characteristic of a reversible response is obtained. At higher frequencies, curvature consistent with quasireversibility is observed. The calculated value of k_s, assuming $\alpha = 0.5$, is given in Table III.

These data establish that $Cr(acac)_3$ and $Cr(SacSac)_3$ undergo successive reductions via the generalized mechanism of Scheme I. The rate constant k_1 is important only for $Cr(acac)_3$, which probably reflects the very negative potential at which $Cr(acac)_3^-$ is generated, rather than any basic mechanistic difference between acac and SacSac complexes.

Scheme I



$$\begin{tikzcd} \mathrm{Cr^{III}L_3} \arrow[r, shift left, "k_s"] & \mathrm{Cr^{II}L_3^-} \arrow[l, shift left] \arrow[r, shift left, "k'_s"] \arrow[d, "k_1"] & \mathrm{Cr^{I}L_3^{2-}} \arrow[l, shift left] \arrow[d, "k_2"] \\ & \text{product} & \text{product}' \end{tikzcd}$$

Table II. Voltammetric Behavior of the First Reduction Waves of the Complexes[e]

	$Cr(acac)_3$	$Mn(acac)_3$	$Fe(acac)_3$	$Co(acac)_3$	$Cr(SacSac)_3$	$Fe(SacSac)_3$	$Co(SacSac)_3$
$E_{1/2}$(Hg), V	−1.72	+0.028	−0.576	−0.250[a]	−0.493	−0.23[b]	−0.7[c]
$E_{1/2}$(Pt), V							
20 mV sec^{-1}		−0.27	−0.590	−0.81	−0.487		−0.649[d]
100 mV sec^{-1}		−0.30	−0.600	−0.92	−0.492		−0.668[d]
$\lvert E_c - E_a \rvert$(Pt), mV							
20 mV sec^{-1}		240	85		70		56.5[d]
100 mV sec^{-1}		465	135		75		78[d]

[a] $E_{1/2}$(Hg) determined over the concentration range 4.62×10^{-5} to 9.23×10^{-4} *M*. [b] From ref 14; corrected by comparison with shift in the $Cr(SacSac)_3$ value. [c] From ref 15. [d] S. V. Evans, A. R. Hendrickson, and R. L. Martin, unpublished results. [e] Dc Polarographic data at controlled drop time of 4.93 sec. $Cr(acac)_3$ value from ac polarography.

Table III. Parameters calculated for the complexes

Compd	10^5D, cm^2 sec^{-1}	α	10^2 k_s(Hg),[a] cm sec^{-1}	10^3 k_s(Pt),[b] cm sec^{-1}
$\mathrm{Cr(SacSac)_3}$	2.4	0.46	>100	19
$\mathrm{Cr(acac)_3}$		0.5[c]	2.3	
$\mathrm{Mn(acac)_3}$	2.6	0.5[c]	6.8	<0.9
$\mathrm{Fe(acac)_3}$	2.6	0.5[c]	13	7.2
$\mathrm{Co(acac)_3}$	2.0	0.5[c]		

[a] k_s(Hg) determined by ac polarography at a controlled drop time of 4.93 sec. [b] k_s(Pt) determined by cyclic voltammetry at a scan rate of 20 mV sec^{-1}. [c] Assumed (see text).

At the shorter time scale of rapid-drop or high-frequency ac experiments, this k_1 step is no longer observed. Plots of $E_{1/2}$ vs. $\sum\sigma$ (sum of Taft substituent coefficients) for both reductions of a series of tris(β-diketonato)chromium(III) complexes are approximately parallel,[33] implying that the overall stereochemistry of the complexes is retained upon successive reductions.

Substitution of sulfur for oxygen shifts both reductions to more positive potentials and enhances the rate of charge transfer. In the absence of double-layer corrections, the large difference in $E_{1/2}$ produced by altering the donor atom precludes quantitative comparisons of k_s values.[32] Even so, the present trend $k_s(\mathrm{O}) < k_s(\mathrm{S})$ is also observed with the analogous divalent nickel complexes where the change in $E_{1/2}$ upon altering the donor atom is much smaller.[34]

Manganese. For $\mathrm{Mn(acac)_3}$ both oxidation (complex wave, centered at ~+0.6 V) and reduction waves were observed at a DME, the $E_{1/2}$ of the latter wave being drop-time dependent (Table I).

The reduction process was sensitive to traces of oxygen and to the working electrode material, as evidenced by cyclic voltammetry at mercury, platinum, and silver electrodes. No oxidation wave was observed at a platinum electrode, this being consistent with a very slow charge-transfer step. The more negative $E_{1/2}$ observed for the reduction process at platinum compared with mercury can be attributed directly to the relatively small k_s value at this electrode surface (Table III).

Due to the proximity of the oxidation wave to the anodic limit at a DME, it could not be fully characterized; however, the $\mathrm{Mn(acac)_3}$ electrode behavior is consistent with the electron-transfer series

$$[\mathrm{Mn^{IV}(acac)_3}]^+ \xleftarrow{k_s} [\mathrm{Mn^{III}(acac)_3}] \xrightarrow{k_s'} [\mathrm{Mn^{II}(acac)_3}]^-$$

The reduction wave is consistent with the chemical isolation of $\mathrm{Na[Mn(acac)_3]}$,[35] and, in contrast to the chromium chelates, the lack of reversibility seems to be a function only of the small k_s. Unfortunately, attempts to synthesize $\mathrm{Mn(SacSac)_3}$ have, so far, proved to be unsuccessful.

Iron. $\mathrm{Fe(acac)_3}$ undergoes a single, one-electron reduction at a DME, some departure from reversibility being evident. A plot of $[I(\omega t)]_\mathrm{p}$ vs. $f^{1/2}$ deviates from linearity at high frequencies at a DME (Figure 1), enabling k_s to be calculated using $\alpha \approx 0.5$. This value of α is consistent with the polarographic data and is confirmed by the very small drop time dependence of $[E_\mathrm{dc}]_\mathrm{p}$.[36]

Cyclic voltammetry at a platinum electrode at scan rates between 0.02 and 5 V sec^{-1} substantiates the lack of complete reversibility at a platinum surface (Table III). The $E_{1/2}$ value is also dependent upon the electrode material (Tables II and III), reflecting the different k_s values at the different electrode surfaces.

Dissociation of $\mathrm{Fe(acac)_3^-}$ has been demonstrated to be quite slow[37,38] and does not influence electrochemical experiments performed on a rapid time scale. Thus, the redox processes of the two compounds may be represented by

$$\mathrm{Fe(SacSac)_3} \xrightleftharpoons{k_{s_1}} \mathrm{Fe(SacSac)_3^-}$$ [14]

$$\mathrm{Fe(acac)_3} \xrightleftharpoons{k_{s_2}} \mathrm{Fe(acac)_3^-} \xrightarrow{k_1} \mathrm{Fe(acac)_2} + \mathrm{acac^-}$$

where $k_{s_1} > k_{s_2}$.

Cobalt. Two $\mathrm{Co(acac)_3}$ reduction waves are observed at a DME at low concentrations (5×10^{-5} to 9×10^{-4} *M*), the first wave having a concentration-independent $E_{1/2}$ and a limiting current varying linearly with concentration. The second wave ($E_{1/2} \approx -1.77$ V) is almost equal in height to the first (controlled drop 4.93 sec) and is found at approximately the potential reported for the first reduction wave of $\mathrm{Co(acac)_2 \cdot H_2O}$ in acetonitrile.[37] These data yield the diffusion coefficient of Table III. At higher concentrations, the $E_{1/2}$ of the first wave is dependent upon concentration and drop time (Table I). Some perturbation in the current–voltage plateau region is evident in the first wave at high concentrations, but at short drop times one wave only is observed in the region of the first reduction. The shape of the dc polarographic wave is consistent with $\alpha \approx 0.5$ and a slow charge transfer, the assumption of slow charge transfer being validated by ac polarography, where only a small current per unit concentration response is observed, the wave height being essentially frequency independent.

In addition to slow electron transfer, chemical nonreversibility of this electrode process would also seem to arise from loss of $\mathrm{acac^-}$. Cyclic voltammograms at a DME show an anodic wave at $E_\mathrm{p} \approx +0.05$ V, the potential of which is concentration dependent and which has been shown to be due to $\mathrm{acac^-}$ by addition experiments. Murray[37] has demonstrated the possibility of acac loss following $\mathrm{Co(acac)_3}$ reduction. For the mechanism

$$\mathrm{ML_3} + e^- \rightleftharpoons \mathrm{ML_3^-} \xrightleftharpoons{K_1} \mathrm{ML_2} + \mathrm{L^-}$$

an analysis similar to that of Murray, with the assumptions of Nernstian charge transfer and complete dissociation of $\mathrm{ML_3^-}$ to $\mathrm{ML_2}$, yields the relationship $E_{1/2} \propto -\log [\mathrm{L^-}]$. Although the charge transfer of the $\mathrm{Co(acac)_3}$ reduction has been shown to be irreversible, the qualitative effect of added $\mathrm{acac^-}$ is likely to be the same as for Nernstian charge transfer. Thus, the predicted negative shift in $E_{1/2}$ of the $\mathrm{Co(acac)_3}$ reduction with increasing concentration of added Na(acac) is observed (a shift to $E_{1/2} \simeq -0.42$ V being observed at a drop time of 0.5 sec, with the $\mathrm{Co(acac)_3}$ solution saturated with Na(acac)) and provides further confirmation that $\mathrm{acac^-}$ is a product of the reduction.

This first reduction wave is markedly electrode dependent, being shifted cathodically by 600 mV on changing from a mercury to a platinum electrode (Table II). The only other electrode process in the range +1.3 to −1.2 V on platinum is a small oxidation peak observed in cyclic voltammograms at $E_\mathrm{p} = +0.44$ V, this being close to the polarographic $E_{1/2}$ value reported for the oxidation of $\mathrm{Co(acac)_2 \cdot H_2O}$ (+0.32 V).[37] This wave may not be correlated directly with our value at platinum; however, the shift in $E_{1/2}$ on changing electrodes is in the expected direction. The anodic wave of $\mathrm{acac^-}$ observed at a DME involves mercury compound formation, and its counterpart is not observed at a platinum electrode.[39]

These observations are consistent with $\mathrm{Co(acac)_3}$ being reduced by the mechanism of Scheme II and lend support to the mechanism tentatively proposed for the reduction of $\mathrm{Co(SacSac)_3}$.[15] That both $\mathrm{Co(acac)_3^-}$ and $\mathrm{Co(SacSac)_3^-}$ readily dissociate to $\mathrm{Co(acac)_2}$ and $\mathrm{Co(SacSac)_2}$ is consistent with the lability frequently observed for $[\mathrm{Co^{II}(chelate)_3}]^{x+}$ complexes. The complexity of the $\mathrm{Co(acac)_3}$ reduction is perhaps increased by polymerization of the reduction product to form oligomers of the type $[\mathrm{Co(acac)_2}]_4$. In the absence

Scheme II

$$\begin{array}{ll}
L = \text{acac} & L = \text{SacSac} \\
\text{CoL}_3 + e^- \xrightarrow{k_s E^1{}_{1/2}} \text{CoL}_3{}^- & \text{CoL}_3 + e^- \xrightarrow{E^1{}_{1/2}} \text{CoL}_3{}^- \\
\text{CoL}_3{}^- \rightleftharpoons \text{CoL}_2 + L^- & \text{CoL}_3{}^- \rightleftharpoons \text{CoL}_2 + L^- \\
\text{CoL}_2 + e^- \xrightarrow{E^2{}_{1/2}} \text{CoL}_2{}^- & \text{CoL}_2 + e^- \xrightleftharpoons{E^2{}_{1/2}} \text{CoL}_2{}^- \\
\text{CoL}_2 \rightarrow \text{products} & \\
E^2{}_{1/2} < E^1{}_{1/2} & E^2{}_{1/2} \geqslant E^1{}_{1/2}
\end{array}$$

of a complete thermodynamic and kinetic description of the redox and associated reactions, meaningful comparisons of observed $E_{1/2}$ values cannot be made.

Summary and Conclusions

The substitution of oxygen for sulfur produces a negative shift in the reduction potential, $E_{1/2}^{\rm r}$, which is consistent with corresponding trends observed for other metals and ligand atoms.[40,41] A consequence of the more negative $E_{1/2}^{\rm r}$ values of the oxygen chelates is that the products of these reductions are thermodynamically more reactive than those of their sulfur analogs and are therefore more likely to undergo follow-up chemical reactions. Despite the marked differences in $E_{1/2}^{\rm r}$ values, the overall mechanisms of the electrode processes appear to differ little for corresponding oxygen and sulfur chelates. Thus, under favorable conditions, the oxygen chelates are capable of supporting electron-transfer series similar to those of their sulfur analogs.

A further consequence of the change of donor atom is an increase in the rate of the heterogeneous charge transfer such that $k_s(\text{S}) > k_s(\text{O})$. Additionally, the rate constant is larger at a mercury than at a platinum working electrode, i.e., $k_s(\text{Hg}) > k_s(\text{Pt})$. Although the rate constants are not corrected for double-layer effects, these trends seem to be general[34] and not influenced by the magnitude of the potential difference $E_{1/2}(\text{S}) - E_{1/2}(\text{O})$ or by the value of the absolute potential, implying that the observed trends are real.

The k_s dependence upon the donor atom and electrode material is consistent with the electron-transfer step occurring via a bridging mechanism involving the electrode and the donor atom, the inequality $k_s(\text{S}) > k_s(\text{O})$ reflecting the thiophilic natures of mercury and platinum. That the $E_{1/2}$ values of the sulfur chelates are independent of the electrode surface is a consequence of the large k_s values. Even though $k_s(\text{S})$ may depend on the electrode material, the electron transfer is sufficiently fast for $E_{1/2}$ to remain unaltered.

Registry No. Cr(acac)$_3$, 13681-82-8; Mn(acac)$_3$, 14284-89-0; Fe(acac)$_3$, 14024-18-1; Co(acac)$_3$, 13681-88-4; Cr(SacSac)$_3$, 39838-20-5; Co(SacSac)$_3$, 26304-94-9.

References and Notes

(1) R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966).
(2) G. A. Heath, R. L. Martin, and A. F. Masters, *Aust. J. Chem.*, **25**, 2547 (1972).
(3) K. Knauer, P. Hemmerich, and J. D. W. van Voorst, *Angew. Chem., Int. Ed. Engl.*, **6**, 262 (1967).
(4) G. A. Heath, and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970).
(5) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **24**, 2061 (1971).
(6) A. R. Hendrickson and R. L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).
(7) A. Furuhashi, S. Kawai, K. Watanuki, and A. Ouchi, *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo*, **20**, 47 (1970).
(8) R. Beckett, G. A. Heath, B. F. Hoskins, B. P. Kelly, R. L. Martin, I. A. G. Roos, and P. L. Weickhardt, *Inorg. Nucl. Chem. Lett.*, **6**, 257 (1970).
(9) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).
(10) R. K. Y. Ho and S. E. Livingstone, *Aust. J. Chem.*, **21**, 1987 (1968).
(11) M. Cox, J. Darken, B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, and K. A. Rogers, *Chem. Commun.*, 105 (1970).
(12) O. Siiman and J. Fresco, *J. Am. Chem. Soc.*, **92**, 2652 (1970).
(13) (a) E.g., D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); (b) e.g. D. W. Barnum, *ibid.*, **22**, 183 (1961).
(14) A. M. Bond, G. A. Heath, and R. L. Martin, *J. Electrochem. Soc.*, **117**, 1362 (1970).
(15) A. M. Bond, G. A. Heath, and R. L. Martin, *Inorg. Chem.*, **10**, 2026 (1971).
(16) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Am. Chem. Soc.*, **95**, 1449 (1973).
(17) G. N. Schrauzer, *Transition Met. Chem.*, **4**, 299 (1968).
(18) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(19) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rhode, *Aust. J. Chem.*, **27**, 2533 (1973).
(20) F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).
(21) A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).
(22) A. L. Balch, *J. Am. Chem. Soc.*, **91**, 1948 (1969).
(23) P. J. Lingane, *Inorg. Chem.*, **9**, 1162 (1970).
(24) The SacSac compounds were prepared as described in ref 2 and 5. The preparations of the acac compounds were as follows: Cr(acac)$_3$, W. C. Fernelius and J. E. Blanch, *Inorg. Synth.*, **5**, 130 (1957); Mn(acac)$_3$, R. C. Charles, *ibid.*, 7, 183 (1963); Fe(acac)$_3$, D. T. Farrar and M. M. Jones, *J. Phys. Chem.*, **68**, 1717 (1964); Co(acac)$_3$, B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, **5**, 188 (1957).
(25) J. Heyrovský, and J. Kuta, "Principles of Polarography", Academic Press, New York, N.Y., 1966, p 80.
(26) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(27) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).
(28) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).
(29) A. M. Bond, *Anal. Chem.*, **44**, 315 (1972).
(30) A. M. Bond, *J. Electroanal. Chem.*, **35**, 343 (1972).
(31) D. E. Smith and T. G. McCord, *Anal. Chem.*, **40**, 474 (1968).
(32) D. E. Smith, "Electroanalytical Chemistry", Vol. 1, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1966, p 1.
(33) R. F. Handy and R. L. Lintvedt, *Inorg. Chem.*, **13**, 893 (1974).
(34) A. M. Bond, R. L. Martin, and A. F. Masters, to be submitted for publication.
(35) D. P. Graddon and G. M. Mockler, *Aust. J. Chem.*, **17**, 1119 (1964).
(36) D. E. Smith and H. L. Hung, *Anal. Chem.*, **36**, 922 (1964).
(37) R. W. Murray and L. K. Hiller Jr., *Anal. Chem.*, **39**, 1221 (1967).
(38) W. R. Heineman, J. N. Burnett, and R. W. Murray, *Anal. Chem.*, **40**, 1970 (1968).
(39) L. K. Hiller, Jr., J. R. Cockrell, and R. W. Murray, *J. Inorg. Nucl. Chem.*, **31**, 765 (1969).
(40) A. M. Bond, A. T. Casey, and J. R. Thackeray, *Inorg. Chem.*, **13**, 84 (1974).
(41) A. A. Vlček, *Prog. Inorg. Chem.*, **5**, 211 (1963).

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Ring Contributions to the Phosphorus-31 Chemical Shifts of Transition Metal–Phosphorus Chelate Complexes

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Received August 20, 1974 AIC40588X

Recent studies have reported a good linear correlation between the chemical shift of a tertiary phosphine, δ_f, and the change in chemical shift upon coordination to a metal, Δ.[1-3] The coordination shift of a tertiary phosphine can therefore be predicted from the equation $\Delta = A\delta_f + B$ when enough examples are known to calculate values for A and B. This relationship is valid for a variety of transition metal–tertiary phosphine complexes.[1]

The ^{31}P chemical shifts of a number of phosphorus chelate complexes have been reported recently which cannot be predicted from the $\Delta = A\delta_f + B$ relationship.[4-7] This was first explained on the basis of ring strain; however, examination of four-, five-, and six-membered rings revealed a substantially larger degree of deshielding for the five-membered analogs.[6]

We wish herein to compile and compare ^{31}P chemical shift data for three types of phosphorus chelate complexes that exhibit such unusual deshielding effects. Knowledge of the presence and magnitude of such effects can prove to be a valuable aid in making structural assignments.

Discussion of these data is aided by the definition of a new