TABLE II

MOLAR CONDUCTANCE VALUES FOR TETRAHALO(2,4-PENTANEDIONATO)STANNATE(IV) SALTS IN NITROBENZENE

	Λ_m,[a] cm^2 mol^{-1} ohm^{-1}	
	Pyridinium salts	Trimethylammonium salts
[$Cl_4Sn(C_5H_7O_2)$]	17.1 (9.90×10^{-3})	14.8 (1.40×10^{-2})
	19.8 (3.95×10^{-3})	22.5 (2.81×10^{-3})
	25.4 (1.98×10^{-3})	25.3 (5.63×10^{-4})
	26.9 (9.88×10^{-4})	24.5 (1.13×10^{-4})
	29.6 (9.88×10^{-5})	26.4 (2.25×10^{-5})
[$Br_4Sn(C_5H_7O_2)$]	17.0 (9.23×10^{-3})	17.8 (9.44×10^{-3})
	21.5 (1.85×10^{-3})	23.2 (1.89×10^{-3})
	23.4 (3.69×10^{-4})	24.4 (3.78×10^{-4})
	26.9 (7.39×10^{-5})	27.5 (7.55×10^{-5})
		28.8 (1.51×10^{-5})
[$I_4Sn(C_5H_7O_2)$]	13.3 (5.20×10^{-3})	17.0 (8.52×10^{-3})
	14.3 (2.09×10^{-3})	22.0 (1.71×10^{-3})
	15.7 (1.05×10^{-3})	24.9 (3.41×10^{-4})
	16.8 (5.24×10^{-4})	27.4 (6.82×10^{-5})
	20.5 (1.05×10^{-4})	36.6 (1.36×10^{-5})
	29.7 (1.05×10^{-5})	

[a] Molar concentrations are in parentheses.

tuted derivatives $X_2Sn(C_5H_7O_2)_2$ was rejected for several reasons. The possibility of having isolated an $X_3Sn(C_5H_7O_2)$ complex seems remote since no success has been reported in obtaining the monosubstituted derivative by direct reaction of $SnCl_4$ and 2,4-pentanedione.[13] Furthermore, all of the pyridinium complexes isolated melt at substantially higher temperatures than expected for the ammonium halide; *i.e.*, C_5H_5NHCl melts at *ca.* 140°. Also, for a mixture of MX and $X_3Sn(C_5H_7O_2)$ the molar conductivity values should be approximately half those expected for 1:1 electrolytes; all values appear to be in the expected range. The possibility that the new compounds are stoichiometric mixtures of $[M_2][SnX_6]$ and $X_2Sn(C_5H_7O_2)_2$ complexes can be rejected for the following reasons. First, two of the compounds have relatively sharp melting points well above the melting points of the disubstituted product. Second, only a single enolate methyl resonance was observed for each complex in the nmr spectra; all of the disubstituted products have the cis configuration and exhibit two enolate methyl resonances.[6,7] Third, the ^{119}Sn Mössbauer spectra show only a single line of relatively narrow width (see Table I).

Tin-119 Mössbauer spectral data are presented in Table I. Although the complexes do not have cubic symmetry, no quadruple splittings were observed. This fact is consistent with the observations of other workers that octahedrally coordinated nitrogen, oxygen, and halide atoms are not sufficiently different in electrical properties so as to generate significant electrical asymmetry at the tin nucleus.[14] The observed isomer shifts correlate well with the Pauling electronegativity values for the halogens. For the pyridinium series a least-squares analysis generates an equation $IS = -1.26X + 4.46$;[15] for the triethylammonium series the equation is essentially the same.

Attempts were made to extend the reactions of the tin series to germanium and silicon. No analogous anionic complexes were obtained. Reaction of $GeCl_4$, phenyltrichlorogermane, and phenyltrichlorosilane with 2,4-pentanedione and pyridine only led to the isolation of the already characterized disubstituted enolate complexes, *i.e.*, $Cl_2Ge(C_5H_7O_2)_2$,[6b,16] $Cl(C_6H_5)Ge(C_5H_7O_2)_2$,[17] and $Cl(C_6H_5)Si(C_5H_7O_2)_2$;[18] the reaction of $SiCl_4$ with 2,4-pentanedione and pyridine yielded the well-known tris(2,4-pentanedionato)silicon(IV) chloride.[18] Thus the formation of the anionic tetrahalo(2,4-pentanedionato) complexes appears to be specific for tin.

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[13] D. W. Thompson, unpublished results. A 5:1 $SnCl_4$–2,4-pentanedione mixture yields only the disubstituted derivative.

[14] N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc. A*, 1679 (1967).

[15] IS = isomer shift; X = electronegativity value.

[16] T. J. Pinnavaia, L. J. Matienzo, and Y. A. Peters, *Inorg. Chem.*, **9**, 993 (1970).

[17] D. W. Thompson, unpublished results.

[18] R. West, *J. Amer. Chem. Soc.*, **80**, 3247 (1958).

CONTRIBUTION FROM THE E. F. SMITH LABORATORY
OF CHEMISTRY AND LABORATORY FOR RESEARCH ON
THE STRUCTURE OF MATTER, UNIVERSITY OF
PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

Effects of Nitrogen Donors on the Electronic Structure of Cobalt(II) Bis(dithioacetylacetonate)

BY KATHLEEN M. ERCK[1] AND BRADFORD B. WAYLAND*

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The X-ray structure[2] and spectroscopic properties[3,4] of cobalt(II) bis(dithioacetylacetonate), $Co(sacsac)_2$, have been extensively studied since its initial synthesis by Martin and Stewart.[5] The low-spin d^7 complex was shown by epr studies to have a $(d_{xz}, d_{x^2-y^2}, d_{yz})^6(d_{z^2})^1(d_{xy})^0$ ground-state electronic configuration (^2A_g spectroscopic state).[6] An interesting feature of the complex is the large in-plane anisotropy (Table I), which results from the combined effects of a small d_{yz}–d_{z^2} separation ($\Delta E_{yz-z^2} = 1900$ cm^{-1}) and a large d_{xz}–d_{z^2} separation ($\Delta E_{xz-z^2} = 10{,}000$ cm^{-1}). $Co(sacsac)_2$ has recently been reported to form 1:1 adducts with $(C_6H_5)_3M$ (M = P, As, Sb, Bi).[7] Martin and Stewart have noted that, in the absence of air, $Co(sacsac)_2$ gives a green solution in pyridine and correctly suggested that a pyridine complex formed.[5] In this note we wish to report the results of epr and electronic spectral studies of adducts of $Co(sacsac)_2$ with the nitrogen donors piperidine and pyridine and to compare them with the parent $Co(sacsac)_2$ complex. A model for the effects of axial ligation on planar metal chelates originally proposed for Cu(II) chelates[8] has been extended to these adducts of Co(II) complexes.

Results and Discussion

The epr spectra and corresponding parameters for $Co(sacsac)_2$ adducts with piperidine and pyridine are found in Figure 1 and Table I. The splitting of each of the ^{59}Co components in the high-field region into three lines results from the coupling with a single ^{14}N

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[1] NSF trainee, 1969–1971.

[2] R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).

[3] O. Siimann and J. Fresco, *Inorg. Chem.*, **8**, 1846 (1969).

[4] O. Siimann and J. Fesco, *J. Amer. Chem. Soc.*, **92**, 2652 (1970).

[5] R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966).

[6] A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).

[7] J. F. White and M. F. Farona, *Inorg. Chem.*, **10**, 1080 (1971).

[8] B. B. Wayland and A. F. Garito, *ibid.*, **8**, 182 (1969).

Table I

Experimental Epr Parameters for Co(sacsac)$_2$ and 1:1 Adducts with Piperidine and with Pyridine

Co(sacsac)$_2$[a,b]	Co(sacsac)$_2$·pip[b,c]	Co(sacsac)$_2$·py[b,c]
$g_{xx} = 3.280$	$g_1 = 2.48$	$g_1 = 2.49$
$g_{yy} = 1.904$	$g_2 = 2.23$	$g_2 = 2.23$
$g_{zz} = 1.899$	$g_3 = 2.006$	$g_3 = 2.005$
$A_{xx}(^{59}\text{Co}) = 0.0105\ \text{cm}^{-1}$	$A_1(^{59}\text{Co})$ unresolved	$A_1(^{59}\text{Co})$ unresolved
$A_{yy}(^{59}\text{Co}) \approx 0.0035\ \text{cm}^{-1}$	$A_2(^{59}\text{Co}) = 0.0038\ \text{cm}^{-1}$	$A_2(^{59}\text{Co}) = 0.0038\ \text{cm}^{-1}$
$A_{zz}(^{59}\text{Co}) \approx 0.0035\ \text{cm}^{-1}$	$A_3(^{59}\text{Co}) = 0.0053\ \text{cm}^{-1}$	$A_3(^{59}\text{Co}) = 0.0055\ \text{cm}^{-1}$
	$a_{^{14}\text{N}} = 16$ G	$a_{^{14}\text{N}} = 15$ G

[a] A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970). [b] The coordinate system for Co(sacsac)$_2$ is established such that xy defines the plane containing cobalt and the sulfur donor atoms, with the y axis bisecting each chelate ligand. In the adducts, the nitrogen donor is assumed to coordinate along the z axis. [c] Frozen toluene solution.

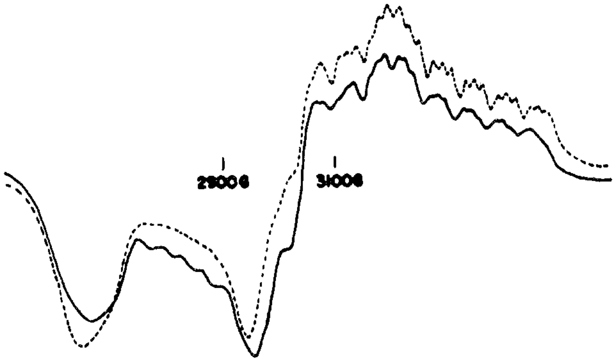

Figure 1.—Epr spectra of Co(sacsac)$_2$·pip (solid line) and Co(sacsac)$_2$·py (broken line) in frozen toluene solution at 130°K.

Table II

Electronic Spectral Data for Co(sacsac)$_2$ and 1:1 Adducts with Piperidine and Pyridine

Co(sacsac)$_2$[a]		Co(sacsac)$_2$·pip[b]		Co(sacsac)$_2$·py[b]	
$\bar{\nu}$, cm^{-1}	ϵ	$\bar{\nu}$, cm^{-1}	ϵ	$\bar{\nu}$, cm^{-1}	ϵ
6,750	20	11,300	50	11,500	50
10,870	30	13,300	~50[c]	13,300[c]	~50
17,500	4,000	17,300	4,200	17,350	4,000
21,600	3,200	21,800	3,500	21,750	3,500
24,000	~5,000	23,700	5,200	23,700	5,200
~28,000	~15,000	26,300	3,500	26,300	3,500
29,400	14,000	28,650	10,000	28,700	10,000
36,600	28,000	35,700	~30,000	35,700	~30,000
40,100	~20,000	39,200	~10,000	39,100	~10,000
44,600	~30,000				

[a] R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966). [b] Toluene solution (298°K). [c] Overlaps intense band centered at 17,300 cm^{-1}.

nucleus and indicates the presence of a 1:1 complex with pyridine and with piperidine.

Assuming a square-pyramidal type structure for the five-coordinate species, such as found for other low-spin Co(II) compounds,[9] and using the relationships described by Maki, *et al.*,[10] a very good fit for the experimental parameters is obtained from calculations based on the $(z^2)^1(xy)^0$ electron configuration. The following equations relate, for this ground state, the observed g and A values with configurational energy separations, ξ the effective spin–orbit coupling parameter, K the Fermi contact interaction term, and P which, like ξ, is proportional to $1/\langle r\rangle^3$ [10]

$$g_{xx} = 2.002 - 6\xi/\Delta E_{yz\rightarrow z^2}$$

$$g_{yy} = 2.002 - 6\xi/\Delta E_{xz\rightarrow z^2}$$

$$g_{zz} = 2.002$$

$$A_{xx} = P[-K - 6\xi/\Delta E_{yz\rightarrow z^2} - {}^1/_7(2 + 3\xi/\Delta E_{xz\rightarrow z^2})]$$

$$A_{yy} = P[-K - 6\xi/\Delta E_{xz\rightarrow z^2} - {}^1/_7(2 + 3\xi/\Delta E_{yz\rightarrow z^2})]$$

$$A_{zz} = P[-K + {}^1/_7(4 + 3\xi/\Delta E_{xz\rightarrow z^2} + 3\xi/\Delta E_{yz\rightarrow z^2})]$$

Results for the piperidine and pyridine adducts are very similar (Tables I and II). The following discussion will be in terms of the piperidine (pip) adduct, although it applies as well to the pyridine adduct.

Having assumed a five-coordinate structure with the nitrogen donor occupying a site on the z axis, the high-field set of resonances ($g = 2.006$) split by the ^{14}N nucleus is taken to correspond to g_{zz}. The g_1 value is taken to be g_{xx}, and g_2 as g_{yy} following the assignments for the parent compound.

Use of the g value relationships and epr parameters for Co(sacsac)$_2$·pip yields $\xi/\Delta E_{xz\rightarrow z^2} = 0.038$ and $\xi/\Delta E_{yz\rightarrow z^2} = 0.079$. The A value relationships were solved for each possible combination of positive and negative A values, and consistent results are obtained only with A_{yy} negative and A_{zz} positive. P is calculated to be 0.017, reduced about 25% from the free-ion value,[11] and K is calculated to be 0.20. Both of these values are easily acceptable in the light of results of other workers for different low-spin Co(II) compounds.[10,12] Using these results, A_{xx} is calculated to be near zero (0.0005 cm^{-1}), which is consistent with lack of A_{xx} resolution in the spectrum.

Reducing ξ, the effective spin–orbit coupling term, from its free-ion value to the same extent as P is reduced gives $\xi = 400$ cm^{-1}. Then $\Delta E_{yz\rightarrow z^2} \cong 5000$ cm^{-1} and $\Delta E_{xz\rightarrow z^2} \cong 10{,}500$ cm^{-1}. The corresponding energy separations in Co(sacsac)$_2$ have been calculated by Martin as $\Delta E_{yz\rightarrow z^2} \cong 1900$ cm^{-1} and $\Delta E_{xz\rightarrow z^2} \cong 10{,}000$ cm^{-1}. The d$_{xz}$–d$_{yz}$ energy separation is clearly reduced in the adduct compared to the parent Co(sacsac)$_2$.

The results of solution electronic spectral studies of the adducts appear in Table II, along with reported values for Co(sacsac)$_2$. In the piperidine and pyridine adducts the transition observed at 13,300 cm^{-1} is tentatively assigned as the d$_{z^2}$ → d$_{xy}$ transition (^{2}A$_1$ → ^{2}A$_2$). The broad band centered around 11,300 cm^{-1} in the adducts may correspond to both d$_{xz}$ → d$_{z^2}$ (^{2}A$_1$ → ^{2}B$_1$) and d$_{x^2-y^2}$ → d$_{z^2}$ (^{2}A$_1$ → ^{2}A$_1$). Results of epr studies place the d$_{xz}$ → d$_{z^2}$ separation at 10,500 cm^{-1}. Observation of the d$_{yz}$ → d$_{z^2}$ (^{2}A$_1$ → ^{2}B$_2$) transition, predicted from epr results to occur at ~5000 cm^{-1}, has been hampered by the presence of C–H overtones in this region.

In Co(sacsac)$_2$ the d$_{z^2}$ → d$_{xy}$ transition (^{2}Ag → ^{2}B$_{1g}$) is of sufficiently high energy (>16,500 cm^{-1}) to be hid-

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(9) M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, 2411 (1970).

(10) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

(11) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **206**, 173 (1951).

(12) A. Abragam, J. Horowitz, and M. H. L. Pryce, *ibid.*, **230**, 169 (1955).

den by the much more intense charge-transfer bands. Of the two low-lying weak bands that do occur in the electronic spectrum of Co(sacsac)$_2$, the band at 10,870 cm^{-1} correlates nicely with the prediction from calculations based on epr data that $d_{xz} \rightarrow d_{z^2}$ ($^2A_g \rightarrow {}^2B_{2g}$) should be seen around 10,000 cm^{-1}. The band at 6750 cm^{-1} may be associated with the $d_{x^2-y^2} \rightarrow d_{z^2}$ ($^2A_g \rightarrow {}^2A_g$) transition, and the low-energy $d_{yz} \rightarrow d_{z^2}$ ($^2A_g \rightarrow {}^2B_{3g}$) transition, predicted by epr results to be $\sim$1900 cm^{-1}, would appear in the infrared region.

The model for effects of axial ligation, originally proposed for Cu(II) chelate complexes,[8] predicts that the principal effects of axial ligation are (1) the d_{xy} is lowered in energy by the metal moving slightly out of the plane of chelate donor atoms, (2) the d_{z^2} is elevated because of interaction with the ligand coordinated along the z axis, and (3) movement of the metal out of the plane destabilizes d_{xz} but has little effect on d_{yz} or $d_{x^2-y^2}$.

The proposed d energy level ordering for Co(sacsac)$_2$ and the 1:1 adduct with piperidine are presented in Figure 2. All experimental observations are consistent with the model. The decrease in d_{xz}–d_{yz} separation determined from the epr parameters is expected from this model. The calculated d_{xz}–d_{z^2} separation remains almost constant which is also compatible, since both levels are destabilized upon adduct formation. The energy of the d_{yz} level is relatively unchanged and so the d_{yz}–d_{z^2} separation increases.

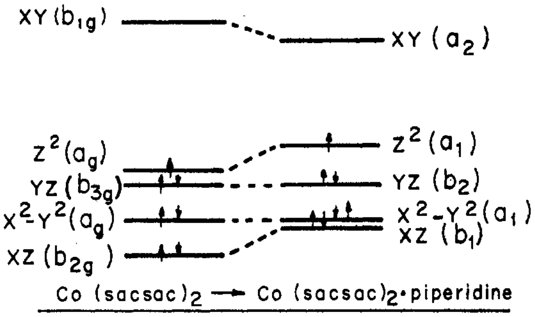

Figure 2.—Proposed d energy level orderings for Co(sacsac)$_2$ and Co(sacsac)$_2$·pip.

The observed effects of axial ligation on the electronic structure of this low-spin Co(II) complex is thus compatible with the model applied to adducts of Cu(II) chelates. These observations encourage further studies to examine the general structural and electronic effects associated with adduct formation of planar transition metal complexes.

Experimental Section

Co(sacsac)$_2$ was prepared according to a previously reported method.[5,13] Elemental analyses for C, H, and S were performed by Galbraith Laboratories, Knoxville, Tenn. *Anal.* Calcd for Co(sacsac)$_2$: C, 37.37; H, 4.40; S, 39.90. Found: C, 37.53; H, 4.45; S, 40.12. The crystalline solid was stored in a desiccator or under vacuum.

Samples were prepared for epr studies on a vacuum line by distilling amine and solvent into quartz tubes containing degassed, solid Co(sacsac)$_2$. Samples were thoroughly degassed and sealed to prevent contact with air. (The solutions are very air sensitive, changing in a matter of seconds from deep green to amber upon contact with air. The adducts in solution must be scrupulously protected from atmospheric contact.) Spectra were collected on a Varian X-band spectrometer. Samples were used as frozen solutions at 130°K, with temperature controlled by a Varian variable-temperature control unit.

Electronic spectra were collected on a Cary 14 spectrophotometer. Samples were prepared from rigorously degassed materials in an inert-atmosphere box filled with an argon–hydrogen mixture and sealed in Infracil cells.

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[13] R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969).

CONTRIBUTION FROM FRICK CHEMICAL LABORATORY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Noble Gas–Boron Compounds[1a]

BY JOEL F. LIEBMAN[1b] AND LELAND C. ALLEN*

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Almost all theoretical and experimental studies on noble gas compounds relate to oxygen and fluorine chemistry.[2] Recently, however, there has been an increased interest in compounds containing noble gas–chlorine,[3] –bromine,[4] and –nitrogen[5] bonds. It is interesting to note that noble gas–boron compounds had been claimed to exist about 30 years ago,[6a] repudiated,[6b] and, finally, definitively synthesized by an indirect reaction.[6c] We have employed LC (Hartree–Fock) AO-MO-SCF wavefunctions to investigate the potential surfaces of $^1\Sigma$ HeB$^+$, $^1\Sigma$ NeB$^+$ and $^1\Sigma$ ArB$^+$, and we compare our results to previously studied fluorine and nitrogen compounds. Connection is made between the diatomic results and other facets of noble gas and boron chemistry.

Methods of Calculation

The potential surfaces of HeB$^+$, NeB$^+$, and ArB$^+$ were obtained using programs developed in this laboratory.[7] The helium atom was represented by five s-type gaussian basis functions contracted to two basis orbitals,[8] neon and boron were represented by ten s-

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[1] (a) Financial support was provided by the Power Branch of the Office of Naval Research, Contract No. N00014-67-A-0151-0016. (b) NSF Predoctoral Fellow, 1968–1970.

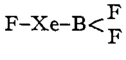
[2] J. F. Liebman and L. C. Allen, *J. Chem. Soc. D*, 1355 (1969); *J. Amer. Chem. Soc.*, **92**, 3539 (1970).

[3] G. J. Perlow and M. R. Perlow, *J. Chem. Phys.*, **41**, 1157 (1964); **48**, 955 (1968).

[4] G. J. Perlow and H. Yoshida, *ibid.*, **49**, 1474 (1968).

[5] W. Kaul and R. Fuchs, *Z. Naturforsch. A*, **15**, 326 (1964); J. F. Liebman and L. C. Allen, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 27 (1971).

[6] (a) H. S. Booth and K. S. Willson, *J. Amer. Chem. Soc.*, **57**, 2273 (1935). (b) E. Wiberg and K. Karbe, *Z. Anorg. Chem.*, **256**, 307 (1948). They also tried to cause Xe and Kr to react with BF$_3$ in the liquid phase but found them almost immiscible. (c) C. T. Goetschel, K. R. Loos, and V. A. Campanile, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1968, No. INOR 213; C. T. Goetschel and K. R. Loos, submitted for publication in *J. Amer. Chem. Soc.* This latter reference gives Raman and ir spectra to prove that the molecule has the structure



$$\mathrm{F\text{-}Xe\text{-}B}{<}^{\mathrm{F}}_{\mathrm{F}}$$

Further work by the same authors shows that the krypton compound also possesses this structure.

[7] S. Rothenberg, P. Kollman, M. E. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem.*, **3S**, 715 (1970).

[8] J. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).