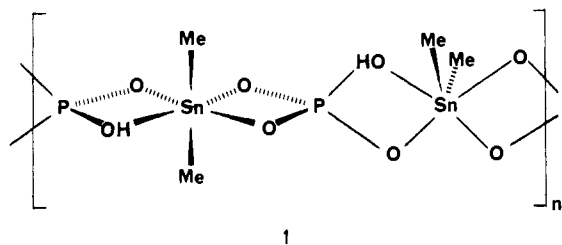


structure. Structure 1 is tentatively proposed on the basis of



analogies to $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and other dimethyltin(IV) compounds, which adopt distorted octahedral geometries at tin.^{7,12-14} In 1 the tin methyls of $\text{Me}_2\text{SnHPO}_4$ lie on either side of a distorted square plane (two long, two short Sn-O bonds) containing tin and four phosphate oxygens. In view of the apparent importance of hydrogen-bonding interactions in other organotin(IV) solids,^{3a,7,15} the linear polymeric chains of $\text{Me}_2\text{SnHPO}_4$ likely associate via hydrogen bonds to produce a two- or three-dimensional network.

Conclusions

Elemental analysis, IR, and solid-state NMR data establish the difference between the usual microcrystalline product of the reaction of Me_2SnCl_2 with Na_2HPO_4 and NaH_2PO_4 and the apparently atypical crystalline product that was previously isolated and characterized by X-ray diffraction. Earlier identifications of the microcrystalline product as $\text{Me}_2\text{SnHPO}_4$ are strongly supported. Further, the tin-carbon J coupling observed in the solid-state ^{13}C NMR spectra of microcrystalline $\text{Me}_2\text{SnHPO}_4$ provides insight into its molecular structure and allows comparison with the structure of X-ray characterized $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ to be made.

Experimental Section

Materials. Me_2SnCl_2 , $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ were obtained from commercial sources and used without purification. Aqueous solutions of Me_2SnCl_2 and Na_2HPO_4 or NaH_2PO_4 were combined at room temperature and allowed to stand undisturbed during product ($\text{Me}_2\text{SnHPO}_4$) formation.^{2,8} At higher concentrations of reagents (0.3 M) a powder (microcrystalline needles or plates) formed shortly after mixing, and precipitation was essentially complete within 24 h; at lower concentrations (to 0.002 M) the product (macroscopic needles) appeared after 1 or more days, and several weeks were required for a good conversion to product. Under no conditions were crystals of $\text{Me}_2\text{SnHPO}_4$ with cross-sections sufficient for X-ray crystallography obtained. The product was isolated by suction filtration and rinsed with methanol. Isolated yields ranged from 50 to 90% for reactant concentrations between 0.3 and 0.03 M. No melting was observed up to temperatures of 340 °C. FT-IR (solid state, diffuse reflectance): 3250 (s, br), 2994 (m), 2906 (m), 2762 (w), 2217 (br, w), 1728 (w), 1600 (w), 1425 (m), 1214 (s), 1193 (s), 1132 (s), 1106 (s), 1054 (br, s), 910 (s), 823 (s), 669 (m), 607 (m), 566 (s) cm^{-1} . All attempts to obtain $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, by varying the concentration of reagents, adjusting the pH between 3 and 7,^{7a} or changing the stoichiometry to 3:2 Me_2SnCl_2 : Na_2HPO_4 (or NaH_2PO_4) provided only $\text{Me}_2\text{SnHPO}_4$.

NMR Spectroscopy. Solid-state ^{13}C NMR spectra were obtained on samples of ca. 0.4 g at 15.08 MHz with a homebuilt instrument with a probe temperature of 304 K. The high-resolution spectra were acquired with 60-MHz high-power proton decoupling, spin-locking cross-polarization with ^1H and ^{13}C fields matched at 57 kHz for 2 ms, and magic angle spinning at 2300 Hz. Dwell times of 50 μs and repetition rates of 9 s were used. ^{13}C chemical shifts are relative to the internal secondary standard Delrin (89.1 ± 0.3 ppm). Spectra revealing chemical shift information could be obtained in about 200 scans; 2-3K scans were required to observe the tin satellites clearly. Because of the similar gyromagnetic ratios of the spin- $1/2$ isotopes ^{117}Sn and ^{119}Sn (1:1.046) and their similar natural abundances (7.6 and 8.6%, respectively), the magnitude of $^1J(^{119}\text{Sn}, ^{13}\text{C})$ was calculated by multiplying the separation of the fused ^{117}Sn and ^{119}Sn satellite resonances by 1.023.

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Acknowledgment. We thank Professor T. Chivers (University of Calgary) for helpful suggestions and for providing us with the IR spectrum of $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and Professor J. J. Zuckerman for a critical reading of this manuscript.

Registry No. ($\text{Me}_2\text{SnHPO}_4$), 100485-80-1; Me_2SnCl_2 , 753-73-1; Na_2HPO_4 , 7558-79-4; NaH_2PO_4 , 7558-80-7.

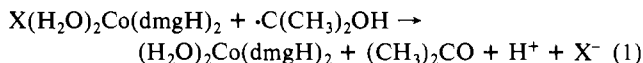
Contribution from Ames Laboratory
and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Flash-Photolytic Study of the Kinetics and Mechanism of the Reduction of Halocobaloximes by 1-Hydroxy-1-methylethyl Radicals¹

Philip Connolly, James H. Espenson,* and Andreja Bakac

Received June 18, 1985

This work was begun with two objectives in mind. First, we sought to study the kinetics of reduction of some members of a family of cobalt(III) complexes by an aliphatic radical; several other examples have been explored,²⁻⁶ but not cobaloximes.⁷ Second, we sought to develop a method that would allow the flash-photolytic formation of the radical and monitoring of product buildup (rather than reactant loss, with its attendant limitations). The α -radical from 2-propanol, $\cdot\text{C}(\text{CH}_3)_2\text{OH}$, seemed like an ideal test case for both objectives, since its chemistry has been widely explored by pulse radiolysis. This radical was found to react with the complexes $\text{X}(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$ ($\text{X} = \text{Cl}, \text{Br}$) as in eq 1.

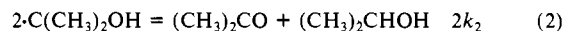


Experimental Section

The complexes $\text{X}(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$ ($\text{X} = \text{Cl}, \text{Br}$) were prepared by the literature method⁸ and characterized by cobalt analysis. Other chemicals were reagent grade materials or standard preparations.

The flash photolysis experiments were performed with the Xenon Corp. Model 710 flash photolysis unit described previously.⁹ The photomultiplier voltages were collected and digitized by a Nicolet Model 2090-3A digital oscilloscope with a Model 206-1 plug-in unit, interfaced with an Apple II computer. The reactions were monitored by recording the growth in absorbance at 462 nm, an absorption maximum of $(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$ (ϵ 3400 $\text{M}^{-1} \text{cm}^{-1}$).¹⁰

The flash photolysis equipment has a dead time of about 70 μs . Since the reactions between $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ and $\text{X}(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$ occur rapidly ($k \approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$), the cobalt(III) concentration must be $< \sim 10^{-4} \text{ M}$. The disproportionation of the radical (eq 2) cannot be avoided,



however, since it has a rate constant $k_2 = 7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ This

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 (7) Cobaloxime is the trivial name given to $\text{Co}(\text{dmgH})_2$ complexes, where dmgH^- is the monoanion of dimethylglyoxime, or 2,3-butanedione di-oxime.
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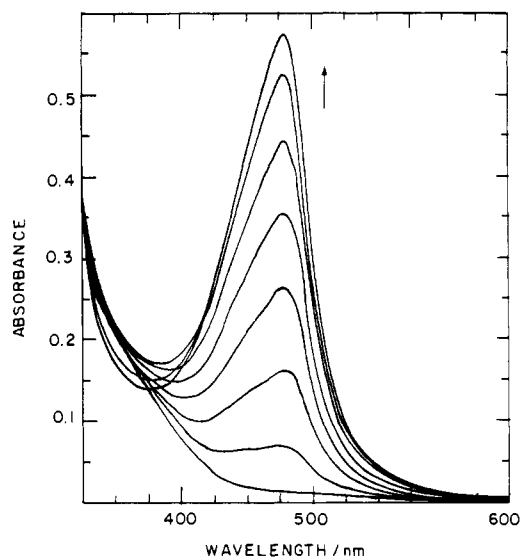


Figure 1. Spectral changes showing the buildup of the 462-nm peak of the cobalt(II) complex $(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$ during the photolysis of 1.9×10^{-4} M $\text{Cl}(\text{H}_2\text{O})\text{Co}(\text{dmgH})_2$ in a solution containing 1 M 2-propanol and 1 M acetone, in a pH 7.5 phosphate buffer. Each scan was taken after a 15-s photolysis time with a 275-W sunlamp.

complication precludes a pseudo-first-order analysis, even though the absorbance change arises from one product of a pseudo-first-order reaction (eq 1).¹²

The kinetic equations for this system, with $\text{R}\cdot = \cdot\text{C}(\text{CH}_3)_2\text{OH}$, are

$$d[\text{Co}^{\text{II}}]/dt = k_1[\text{R}\cdot][\text{X}(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2] \quad (3)$$

$$-d[\text{R}\cdot]/dt = k_1[\text{R}\cdot][\text{X}(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2] + 2k_2[\text{R}\cdot]^2 \quad (4)$$

Integration of eq 4 yields $[\text{R}\cdot]$; substitution of that expression into eq 3, followed by integration, results in the expression for $[\text{Co}^{\text{II}}]_t$:

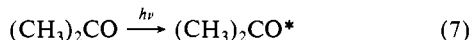
$$[\text{Co}^{\text{II}}]_t = \frac{k_1[\text{Co}^{\text{III}}]}{2k_2} \times \left\{ \ln \left[\frac{(k_1[\text{Co}^{\text{III}}] + 2k_2[\text{R}\cdot]_0)e^{k_1[\text{Co}^{\text{III}}]_t} - 2k_2[\text{R}\cdot]_0}{k_1[\text{Co}^{\text{III}}]} \right] - k_1[\text{Co}^{\text{III}}]_t \right\} \quad (5)$$

A nonlinear least-squares analysis of the kinetic data according to eq 5 gives $k_1[\text{Co}^{\text{III}}]$ for each run. The initial concentration of the radical must be known for the calculation, however, and since it is not directly measured, an iterative process was used.^{1,13} The estimate of $[\text{R}\cdot]_0$ was revised until consistent values of $k_1[\text{Co}^{\text{III}}]$ and $[\text{Co}^{\text{II}}]_\infty$ (from eq 6) were obtained.

$$[\text{Co}^{\text{II}}]_\infty = \frac{k_1[\text{Co}^{\text{III}}]}{2k_2} \left[\ln \left(\frac{k_1[\text{Co}^{\text{III}}] + 2k_2[\text{R}\cdot]_0}{k_1[\text{Co}^{\text{III}}]} \right) \right] \quad (6)$$

Results and Discussion

Photochemistry. The hydroxy-isopropyl radical can be prepared conveniently by the UV irradiation of acetone in the presence of 2-propanol,¹⁴ as in eq 7 and 8. The steady-state photolysis of



a solution of acetone, 2-propanol, and the desired cobalt(III) complex products the absorption spectrum of the cobalt(II) cobaloxime, as in Figure 1. Photolysis of the halocobaloxime in a solution containing only 2-propanol or only acetone does not result in cobalt(II) formation.

The eventual yield of cobalt(II) is 87% of the initial cobalt(III). The losses, most evidence in the spectral region around 400 nm,

Table I. Kinetic Data for the Reduction of Bromoaquocobaloxime by 1-Hydroxy-1-methylethyl Radicals^a

$10^6(\text{concn})/\text{M}$					
$[\text{BrCo}^{\text{III}}]_{\text{av}}^b$	$[\text{R}\cdot]_0^d$	$[\text{Co}^{\text{II}}]_\infty^c$ (obsd)	$[\text{Co}^{\text{II}}]_\infty^c$ (calcd) ^d	$10^{-3}k_{\text{obsd}}/$ s^{-1}	$10^{-8}k_{\text{Br}}/$ $\text{M}^{-1}\text{s}^{-1e}$
8.98	11.2	2.04	2.66	0.96	1.1
9.15 ^c	5.23	1.70	1.92	1.40	1.5
13.9	5.22	2.26	2.35	1.91	1.4
14.2 ^c	2.22	1.42	1.41	2.66	1.9
14.9 ^c	5.39	2.43	2.47	1.66	1.1
18.3	10.9	3.40	3.93	2.16	1.2
23.5	5.04	3.01	2.86	3.65	1.5
23.9 ^c	2.82	2.26	1.94	4.44	1.9
24.4 ^c	5.39	2.82	3.02	2.40	1.0
24.9 ^c	5.39	3.93	3.07	3.88	1.6
27.7	10.7	4.65	4.77	3.76	1.4
29.7 ^c	7.85	4.66	4.13	4.90	1.6
33.1	5.48	3.80	3.41	5.45	1.7
37.2	10.5	5.57	5.37	5.39	1.5
38.8 ^c	2.84	2.30	2.19	5.19	1.3
46.7	10.7	6.66	5.94	8.42	1.8
					1.5 ± 0.2 (av)

^a At 23 ± 1 °C in pH 7.5 phosphate buffer. ^b $[\text{BrCo}^{\text{III}}]_{\text{av}} = [\text{BrCo}^{\text{III}}]_0 - 0.5([\text{Co}^{\text{II}}]_\infty(\text{obsd}))$. ^c At 23 ± 1 °C in pH 8 acetate medium. ^d Refined value by iterative technique (see text). ^e $k_{\text{obsd}}/[\text{BrCo}^{\text{III}}]_{\text{av}}$.

Table II. Kinetic Data for the Reduction of Chloroaquocobaloxime by 1-Hydroxy-1-methylethyl Radicals^a

$10^6(\text{concn})/\text{M}$					
$[\text{ClCo}^{\text{III}}]_{\text{av}}^b$	$[\text{R}\cdot]_0^d$	$[\text{Co}^{\text{II}}]_\infty^c$ (obsd) ^d	$[\text{Co}^{\text{II}}]_\infty^c$ (calcd) ^d	$10^{-3}k_{\text{obsd}}/$ s^{-1}	$10^{-7}k_{\text{Cl}}/$ $\text{M}^{-1}\text{s}^{-1e}$
18.8	9.36	2.50	2.71	1.63	8.7
28.7	5.08	2.55	2.48	2.88	10.0
37.4	19.9	5.26	5.55	3.18	8.5
47.4	15.2	5.24	5.59	4.06	8.6
56.6	19.9	6.72	6.99	4.87	8.6
76.6	15.0	6.82	7.01	6.65	8.7
77.2	10.0	5.57	5.53	7.30	9.5
					8.9 ± 0.6 (av)

^{a-e} See the corresponding footnotes in Table I.

occur in the final stages of photolysis. This probably arises from a reaction of $\cdot(\text{CH}_3)_2\text{OH}$ with the $(\text{dmgH})_2$ ligand system of the Co(II) product. When Co(III) is present in substantial excess, as in the kinetic determinations, this is unimportant.

Kinetics. The data, evaluated as described above, are given in Tables I and II. Cobaloxime concentrations were $(1-8) \times 10^{-5}$ M. Comparable results were obtained in acetate (pH 8) and phosphate (pH 7.5) buffers. This analysis yields the following rate constants: $k_1(\text{Cl}) = (8.9 \pm 0.6) \times 10^7$ and $k_1(\text{Br}) = (1.5 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 23 ± 1 °C.

Reaction Mechanism. If an inner-sphere mechanism operates, the immediate product would be the α -halo alcohol, $\text{XCH}(\text{CH}_3)_2\text{OH}$, which would rapidly produce acetone + $\text{HX}(\text{aq})$. Alternatively, the reaction could occur by outer-sphere electron transfer, yielding the same products directly.

Precedents for both can be cited. Cyclopentyl¹⁵ and 2-propyl radicals¹⁶ react with $(\text{NH}_3)_5\text{CoBr}^{2+}$ to yield the corresponding alkyl bromides, thus providing direct proof of halogen atom abstraction. The reaction of alkyl radicals with IrCl_6^{2-} occurs by parallel inner-sphere and outer-sphere pathways,^{17,18} the former yielding RCl and the latter ROH . In addition, copper(II) complexes show an increasing tendency toward direct atom transfer to an alkyl radical as opposed to direct attack at the metal center as the radical is changed from methyl to ethyl to 2-propyl.¹⁹

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The reactions of $\text{-C(CH}_3)_2\text{OH}$ with $(\text{NH}_3)_5\text{CoX}^{2+}$ complexes were believed to favor an X-bridged transition state because of the large variations in rate with different groups X.² The reactivity ratio $k_{\text{Br}}/k_{\text{Cl}}$ is 7.5, whereas it is 1.7 for eq 1. The smaller selectivity here as compared to that for the pentaamine complexes may indicate a change to an outer-sphere mechanism. This is not unprecedented, since it has been suggested that this should be the preferred mechanism.¹⁸ It is possible also that the low-lying π^* orbitals of the oxime ligand²⁰ are involved in facilitating electron transfer to cobalt. Finally, it should be noted that the reductions of similar cobalt(III) macrocycles, $\text{XCo}(\text{Me}_4[14]\text{tetaeneN}_4)$ and

$\text{XCo}(\text{Me}_4[14]4,11\text{-dieneN}_4)$, also showed small changes in rate for various axial ligands, H_2O , OH^- , and Cl^- .²¹ In the final analysis, the data are more suggestive of an outer-sphere electron-transfer process than otherwise, but the situation does not admit of a definitive formulation.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $\text{Cl}(\text{H}_2\text{O})\text{Co}(\text{dmgH})_2$, 22898-86-8; $\text{Br}(\text{H}_2\text{O})\text{Co}(\text{dmgH})_2$, 26493-68-5; $(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$, 37115-10-9; $\text{-C(CH}_3)_2\text{OH}$, 5131-95-3; $\text{HC(CH}_3)_2\text{OH}$, 67-63-0; $(\text{CH}_3)_2\text{CO}$, 67-64-1.

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Additions and Corrections

1985, Volume 24

Susan J. Berners Price, Michael J. DiMartino, David T. Hill, Reiko Kuroda, Muhammed A. Mazid, and Peter J. Sadler*: Tertiary Phosphine Complexes of Gold(I) and Gold(III) with Imido Ligands: ^1H , ^{31}P , and ^{15}N NMR Spectroscopy, Antiinflammatory Activity, and X-ray Crystal Structure of (Phthalimido)(triethylphosphine)gold(I).

Pages 3425–3434. The space group reported for the title complex $\text{Et}_3\text{PAu}(\text{ptm})$ is incorrect. It should be $Pcmm$ (No. 62). The structure has now been recalculated. The change of space group leads to only minor changes in bond lengths and angles. The essential features of the

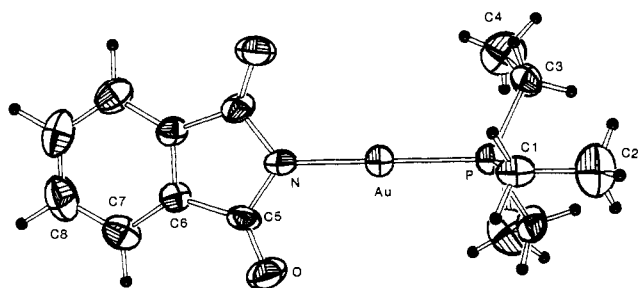


Figure 2. Revised molecular structure of (phthalimido)(triethylphosphine)gold(I) and numbering system. The space group imposes a mirror plane of symmetry through N, Au, P, C1, C2, and H2A perpendicular to the page.

Table I. Unit Cell Positional and Thermal Parameters with Estimated Standard Deviations in Parentheses

atom	x	y	z	$B_{\text{eq}},^a \text{ \AA}^2$
Au	-0.15373 (6)	0.250	-0.14532 (6)	2.92 (1)
P	-0.3321 (4)	0.250	-0.0604 (3)	2.75 (7)
O	0.0368 (7)	0.4570 (7)	-0.2406 (8)	4.9 (2)
N	0.008 (1)	0.250	-0.223 (1)	3.0 (3)
C1	-0.462 (1)	0.250	-0.146 (1)	3.4 (3)
C2	-0.587 (2)	0.250	-0.090 (2)	5.4 (5)
C3	-0.353 (1)	0.384 (1)	0.0208 (8)	3.8 (2)
C4	-0.246 (2)	0.419 (1)	0.089 (1)	6.0 (3)
C5	0.072 (1)	0.3526 (9)	-0.2546 (9)	3.1 (2)
C6	0.1852 (8)	0.3112 (9)	-0.3067 (8)	2.7 (2)
C7	0.282 (1)	0.378 (1)	-0.349 (1)	4.0 (2)
C8	0.377 (1)	0.311 (1)	-0.396 (1)	5.7 (3)

$$^a B_{\text{eq}} = (4/3)(a^2 B_{11} + b^2 B_{22} + c^2 B_{33}).$$

Table II. Bond Distances (\AA) and Angles (deg) with Estimated Standard Deviations in Parentheses^a

Au–P	2.239 (2)	C1–C2	1.551 (14)
Au–N	2.030 (7)	C3–C4	1.513 (11)
P–C1	1.800 (10)	C5–C6	1.480 (8)
P–C3	1.814 (6)	C6–C6'	1.349 (11)
O–C5	1.227 (7)	C6–C7	1.404 (8)
N–C5	1.395 (7)	C7–C8	1.418 (9)
		C8–C8'	1.34 (2)
P–Au–N	179.8 (3)	O–C5–N	123.8 (8)
Au–P–C1	114.0 (4)	O–C5–C6	128.3 (6)
Au–P–C3	112.7 (2)	N–C5–C6	107.8 (5)
C1–P–C3	104.0 (3)	C5–C6–C6'	108.0 (3)
C3–P–C3'	108.7 (4)	C5–C6–C7	130.1 (6)
Au–N–C5	125.8 (4)	C6'–C6–C7	121.9 (4)
C5–N–C5'	108.3 (7)	C6–C7–C8	116.3 (6)
P–C1–C2	115.3 (8)	C7–C8–C8'	121.7 (4)
P–C3–C4	115.4 (6)		

^a Primed atoms are related by a mirror plane to the corresponding unprimed atoms.

structure remain the same, and none of the discussion is affected. Revised versions of Figure 2 and Tables I and II are shown here.

The Au, P, N, C1, C2, and H2A atoms are on a mirror plane. All the non-hydrogen atoms have been refined anisotropically without any constraint on the geometry. Five (H1, H2A, H3A, H3B, and H4A) of the ten hydrogen atoms were generated by assuming ideal geometry. The positional and isotropic thermal parameters of the hydrogen atoms were not included in the refinement. The final R value is 0.034, and the maximum shift/error is 0.08. The final difference Fourier map did not contain any residual electron density $>0.749 \text{ e \AA}^{-3}$.

We are very grateful to Dr. P. G. Jones (University of Göttingen) for his suggestion that we reexamine the assignment of the space group and for his critical comments on this correction.

Supplementary Material Available: Revised tables of observed and calculated structure factors, anisotropic thermal parameters, and coordinates of hydrogen atoms (7 pages). Ordering information is given on any current masthead page.—Peter J. Sadler

1986, Volume 25

Shigeru Tsuruya,* Shun-ichi Yanai, and Mitsuo Masai: Cobalt(II) Chelate Catalyzed Oxidation of 3,5-Di-*tert*-butylcatechol.

Page 145. In Table V, the headings H and S should be ΔH^\ddagger and ΔS^\ddagger , respectively.—Shigeru Tsuruya