Table V. Relevant Bond Distances (Å) and Angles (deg) in Tc(V) Octahedral Oxo Complexes with Esd's in Parentheses

compound	$d_{Tc-O_{oxo}}$	$d_{Tc-O_{trans}}$	O(trans) belonging to	mean angle O_{oxo}–Tc–L_{cis}	Δ^a	ref
$TcOBr_2(OEt)(Npy)_2$	1.684 (6)	1.855 (6)	$R-O^-$	91.1 (3)	0.05	39
$TcOCl(oxMe)_2$	1.649 (3)	1.994 (3)	$Ar-O^-$	96.2 (1)	0.22	17
$TcO(pam)_2$	1.657 (4)	2.214 (4)	$R-COO^-$	100.9 (2)	0.42	40
$\{TcO(H_2O)[(acac)_2en]\}^+$	1.648 (2)	2.282 (2)	H_2O	100.7 (1)	0.37	15
TcO(Glusal)(sal)	1.656 (8)	2.359 (8)	Ar–CHO	102.4 (4)	0.42	this work

[a] Δ = displacement of the Tc atom from the mean plane of the cis ligands toward O_{oxo}. oxMe = 2-methyl-8-quinolate; $(acac)_2en$ = *N,N'*-ethylenebis(acetylacetone iminato); Npy = 4-nitropyridine; pam = D-penicillaminato.

Schiff base ligand (Figure 2). Thus, the coordination mode of sal^- in TcO(Glusal)(sal) appears to be kinetically controlled, and the steric requirements of the tridentate $Glusal^{2-}$ ligand presumably prevent sal^- from rearranging to the thermodynamically more favored coordination mode.

Acknowledgment. Partial support for this work was provided by the National Institutes of Health through Grants HL-21276 and CA-42179. Financial support was also provided by the Italian Consiglio Nazionale delle Richerche. Helpful conversations with Dr. Jean-Luc Vanderheyden and Bruce Wilcox are gratefully acknowledged.

Registry No. TcO(Glusal)(sal), 108343-78-8; $GlusalH_2$, 19124-29-9; $[As(C_6H_5)_4][TcOCl_4]$, 97101-52-5.

Supplementary Material Available: Complete listings of bond distances and angles and tables for anisotropic thermal parameters, hydrogen atom positional parameters, and least-squares planes (6 pages); a table of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Interruption of Conjugation in Transition-Metal-Bound Polyenes: A Reinvestigation of the X-ray Crystal Structure of (Hexamethylbenzene)tricarbonylchromium

Brien P. Byers and Michael B. Hall*

Received November 19, 1986

Table I. Crystallographic Data

formula	$C_{13}H_{18}CrO_3$
fw	298.30
cryst system	orthorhombic
space group	*Pbca*
syst absences	$0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$
a	13.622 (1) Å
b	13.369 (2) Å
c	15.162 (3) Å
vol	2761.2 Å^3
Z	8
d_{calcd}	1.43 g·cm^{-3}
data collection instrument	Enraf-Nonius CAD-4
radiation (graphite monochromated)	Mo Kα (λ = 0.71073 Å)
cryst–detector dist	21 cm
detector aperture	2.0–2.6 mm horiz; 2.0 mm vert
scan type	ω–θ
scan rate	2–20°/min (in ω)
scan width	(0.7 + 0.350 tan θ)°
max 2θ	60°
no. of unique reflcns	4024
high peak in final diff map	0.28 (6) e/Å
temp	177 ± 1 K

refinement	full data	high angle
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2571	1076
no. of params refined	245	172
R_1[a]	0.031	0.025
R_2[b]	0.046	0.032
esd of an observn of unit wt	1.32	0.793

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum(F_o)$. [b] $R_2 = (\sum[w(|F_o| - |F_c|)^2]/\sum[w(|F_o|)^2])^{1/2}$; $w = 4(F_o)^2/\sigma^2(F_o^2)$.

The lowering of symmetry in polyenes π-bound to transition metals and transition-metal fragments has been the subject of controversy for over 20 years.[1] As the accuracy of X-ray crystallographic investigations improve, more accurate values for C–C bond lengths may be determined in polyene rings of organometallic compounds. Early room-temperature X-ray crystallographic studies of $(C_6H_6)Cr(CO)_3$ showed equal C–C bond lengths, within experimental error, in the complexed benzene ring.[2,3] However, a more accurate low-temperature study, which combined X-ray and neutron diffraction, showed C–C bond length alternation.[4] The average difference was 0.017 (2) Å. A low-temperature X-ray study of $(C_6(CH_3)_6)Mo(CO)_3$ indicated that the bond length differences in this analogue averaged 0.036 (9) Å,[5] twice the value seen for $(C_6H_6)Cr(CO)_3$. It has been postulated[6] that long–short C–C bond length alternation should be seen for all $(C_6R_6)M(CO)_3$ (M = Cr, Mo, W) complexes. Small C–C bond length alternation has also been observed in X-ray crystallographic studies of $(C_5(CH_3)_5)M(CO)_2$ (M = Co,[7] Rh[8]) and $(C_5H_5)M(CO)_3$ (M = Mn,[9a] Re[9b]). In almost all cases, room-temperature X-ray studies[2,3,7,8,9] of these and similar complexes have not detected any consistent polyene distortion. The increased accuracy of the low-temperature studies is due to reduction of the carbon atom thermal motions, which obscure their exact positions in room-temperature X-ray studies.

Since an earlier room-temperature X-ray study of $(C_6(CH_3)_6)Cr(CO)_3$ showed no polyene ring distortion,[10] we decided

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(1) (a) Jellinek, F. *J. Organomet. Chem.* **1963**, *1*, 43. (b) Jellinek, F. *Nature (London)* **1960**, *187*, 871. (c) Cotton, F. A.; Dollase, W. A.; Wood, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 1543. (d) Ibers, J. A. **J. Chem. Phys.** *1964*, *40*, 3129.

(2) (a) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 2271. (b) Corradini, P.; Allegra, G. *Atti Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1959**, *26*, 511. (c) Allegra, G. *Atti Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1961**, *31*, 241.

(3) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314.

(4) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1973, *B29*, 2515.

(5) Chesick, J. P.; Koshland, D. E.; Myers, S. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2013.

(6) Chinn, J. W.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930.

(7) Byers, L. F.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277.

(8) Lichtenberger, D. L.; Blevins, C. H., II; Ortega, R. B. *Organometallics* **1984**, *3*, 1614.

(9) (a) Fitzpatrick, P. J.; Le Page, Y.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852. (b) Fitzpatrick, P. J.; Le Page, Y.; Butler, I. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1052.

(10) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298.

0020-1669/87/1326-2186$01.50/0

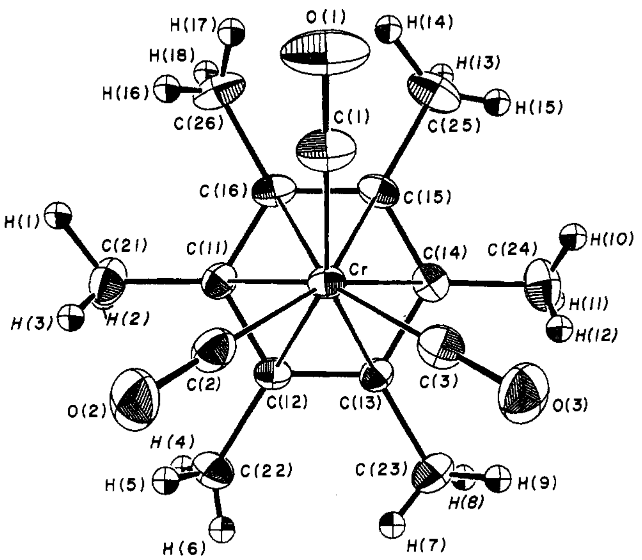

Figure 1. ORTEP plot of $(C_6(CH_3)_6)Cr(CO)_3$.

Table II. Bond Distances (Å) and Selected Angles (deg) for $(C_6(CH_3)_6)Cr(CO)_3$: High-Angle Refinement Values[a]

	Distances		
Cr–C1	1.832 (3)	C11–C12	1.432 (4)
Cr–C2	1.836 (3)	C11–C16	1.411 (4)
Cr–C3	1.840 (3)	C11–C21	1.512 (4)
Cr–C11	2.250 (3)	C12–C13	1.413 (3)
Cr–C12	2.240 (3)	C12–C22	1.509 (4)
Cr–C13	2.236 (2)	C13–C14	1.437 (4)
Cr–C14	2.237 (3)	C13–C23	1.503 (4)
Cr–C15	2.239 (3)	C14–C15	1.415 (4)
Cr–C16	2.244 (3)	C14–C24	1.510 (4)
O1–C1	1.155 (5)	C15–C16	1.432 (4)
O2–C2	1.155 (5)	C15–C25	1.507 (4)
O3–C3	1.155 (5)	C16–C26	1.502 (4)
	Angles		
C1–Cr–C2	89.5 (2)	Cr–C1–O1	177.7 (4)
C1–Cr–C3	89.6 (2)	Cr–C2–O2	178.8 (4)
C2–Cr–C3	89.0 (1)	Cr–C3–O3	179.5 (3)
Cr–C11–C21	131.7 (2)	C13–Cr–C14	37.5 (1)
Cr–C12–C22	130.3 (2)	C12–Cr–C13	36.81 (8)
Cr–C13–C23	130.3 (2)	C11–Cr–C12	37.21 (9)
Cr–C14–C24	130.6 (2)	C16–Cr–C11	36.6 (1)
Cr–C15–C25	130.5 (2)	C16–Cr–C15	37.3 (1)
Cr–C16–C26	130.6 (2)	C15–Cr–C14	36.9 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

to reinvestigate the X-ray crystal structure of $(C_6(CH_3)_6)Cr(CO)_3$ at low temperature. Crystallographic data for the structure are presented in Table I. Shown in Figure 1 is an ORTEP diagram of the structure, indicating $(C_6(CH_3)_6)Cr(CO)_3$ adopts a staggered conformation in the crystal, as does $(C_6H_6)Cr(CO)_3$ and $(C_6(CH_3)_6)Mo(CO)_3$. The results of this study are based on a high-angle ($(\sin \theta)/\lambda > 0.55$ Å^{-1}) refinement of the low-temperature data. It has been found that high-angle data, which emphasize core-electron scattering, reduce some of the bias in the X-ray parameters, yielding thermal parameters lower than those obtained in a full refinement of the data.[11] In the earlier room-temperature photographic study of $(C_6(CH_3)_6)Cr(CO)_3$, R values of $R_1 = 0.105$ and $R_2 = 0.100$ were determined. In this high-angle study we obtained substantially better R values of $R_1 = 0.025$ and $R_2 = 0.032$, for 1076 unique data with $F_o^2 > 3\sigma(F_o^2)$. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropically.

The C–C bond lengths determined at 177 K for the hexamethylbenzene ring, as well as some selected bond angles, are listed in Table II. The average C–C bond length difference in the hexamethylbenzene ring of $(C_6(CH_3)_6)Cr(CO)_3$ is 0.021 (4) Å. Positional and isotropic equivalent thermal parameters are given in Table III. The methyl groups are displaced 0.033 (13) Å out of the plane of the hexamethylbenzene ring away from the Cr atom. This value may be compared to the value of 0.060 (17) Å observed for the methyl displacement in $(C_6(CH_3)_6)Mo(CO)_3$.

Table III. Positional and Isotropic Equivalent Thermal Parameters for $(C_6(CH_3)_6)Cr(CO)_3$: High-Angle Refinement Values[a]

atom	x	y	z	β, Å^2
Cr	0.19230 (2)	0.24584 (2)	0.42367 (2)	1.473 (3)
O1	0.2042 (4)	0.4008 (2)	0.5651 (2)	4.31 (7)
O2	0.3480 (2)	0.3527 (2)	0.3213 (2)	3.56 (4)
O3	0.0404 (2)	0.3665 (2)	0.3285 (2)	3.13 (3)
C1	0.1986 (3)	0.3423 (2)	0.5094 (2)	2.52 (4)
C2	0.2877 (2)	0.3123 (2)	0.3614 (2)	2.04 (3)
C3	0.0988 (2)	0.3201 (2)	0.3655 (2)	2.03 (3)
C11	0.2915 (2)	0.1132 (2)	0.4435 (1)	1.76 (3)
C12	0.2379 (2)	0.1004 (2)	0.3630 (1)	1.70 (3)
C13	0.1343 (2)	0.1055 (1)	0.3626 (1)	1.62 (3)
C14	0.0825 (2)	0.1235 (2)	0.4436 (1)	1.84 (3)
C15	0.1356 (2)	0.1363 (2)	0.5230 (2)	1.97 (3)
C16	0.2407 (2)	0.1315 (2)	0.5229 (1)	1.87 (3)
C21	0.4020 (2)	0.1035 (2)	0.4426 (2)	2.69 (4)
C22	0.2941 (2)	0.0795 (2)	0.2791 (2)	2.63 (4)
C23	0.0771 (2)	0.0901 (2)	0.2790 (2)	2.60 (4)
C24	−0.0283 (2)	0.1262 (2)	0.4433 (3)	2.80 (4)
C25	0.0832 (3)	0.1532 (3)	0.6093 (2)	3.24 (5)
C26	0.2948 (2)	0.1435 (2)	0.6086 (2)	2.69 (4)
H1	0.446 (3)	0.154 (3)	0.492 (3)	12 (1)*
H2	0.413 (2)	0.044 (3)	0.437 (2)	9 (1)*
H3	0.432 (2)	0.137 (3)	0.406 (2)	9 (1)*
H4	0.328 (2)	0.016 (2)	0.282 (2)	4.0 (6)*
H5	0.337 (2)	0.137 (2)	0.269 (2)	5.8 (7)*
H6	0.284 (3)	0.080 (3)	0.228 (3)	11 (1)*
H7	0.118 (2)	0.099 (2)	0.233 (2)	6.9 (8)*
H8	0.036 (2)	0.026 (2)	0.276 (2)	5.0 (7)*
H9	0.021 (2)	0.141 (2)	0.273 (2)	4.5 (6)*
H10	−0.047 (2)	0.177 (2)	0.478 (2)	9 (1)*
H11	−0.050 (2)	0.071 (3)	0.439 (2)	9 (1)*
H12	−0.037 (3)	0.157 (3)	0.401 (3)	12 (1)*
H13	0.068 (2)	0.096 (2)	0.641 (2)	7.5 (9)*
H14	0.134 (3)	0.208 (3)	0.648 (2)	8.2 (9)*
H15	0.022 (2)	0.163 (2)	0.599 (2)	6.3 (8)*
H16	0.344 (2)	0.177 (2)	0.600 (2)	4.6 (6)*
H17	0.283 (2)	0.201 (2)	0.644 (2)	6.3 (8)*
H18	0.311 (2)	0.082 (2)	0.643 (2)	5.9 (8)*

[a] Starred values indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

The C–C bond length alternation of 0.021 (4) Å seen in this study is only 0.004 Å larger than the average bond length difference of 0.017 (2) Å observed for $(C_6H_6)Cr(CO)_6$, but it is 0.015 Å smaller than the difference of 0.036 (9) Å observed for $(C_6(CH_3)_6)Mo(CO)_3$. Thus, substitution of the metal atom in the $(C_6R_6)M(CO)_3$ complexes causes a larger distortion than substitution of the R group. The change observed when substituting Mo for Cr is nearly 4 times that observed when substituting C_6H_6 with $C_6(CH_3)_6$. Intermolecular contacts determined in this study show that the Cr analogue is more tightly packed than the Mo analogue of $(C_6(CH_3)_6)M(CO)_3$. Because the more tightly packed species shows much less polyene ring distortion, it seem likely that packing forces are not the cause of the distortion, as suggested earlier.[10] Further evidence that this distortion is not packing comes from the fact that all C–CH_3 distances are essentially equal.

Theoretical studies[6,12] indicate that mixing of the π-bonding e_{1g} and π-antibonding e_{2u} orbitals of the benzene and hexamethylbenzene rings in the primarily metal molecular orbitals of the (π-polyene)M(CO)$_3$ complex causes the distortion. Thus we would expect more e_{1g}–e_{2u} mixing in $(C_6(CH_3)_6)Mo(CO)_3$ than in the Cr analogue, because of the larger M–C overlap in 4d metals

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[11] Coppens, P. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1975**, *11*, 21.

[12] Hoffman, R.; Albright, T. A. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

compared to that in 3d metals. The tilting of the methyl groups in the complex is connected with the rehybridization of the carbon atoms of the polyene that are bonding with the metal atom.[5] Therefore, there should be more s character in the Mo–C_{ring} bonds than in the Cr–C_{ring} bonds of the $(C_6(CH_3)_6)M(CO)_3$ complexes.

Although the bond length differences are small, they are certainly significant. We conclude that substitution of the metal atom is a much more important factor than substitution of the polyene ring in causing the distortion. It is expected that the crystal structure of $(C_6(CH_3)_6)W(CO)_3$ should show an even greater C–C bond length difference than the Cr or Mo analogues.[13]

Experimental Section

$(C_6(CH_3)_6)Cr(CO)_3$ was prepared by the method of Mahaffey and Pauson[14] and purified by sublimation in vacuo. Crystals of $(C_6(CH_3)_6)Cr(CO)_3$ were grown by slow evaporation of a benzene solution. To ensure no ligand exchange occurred, between the benzene solvent and hexamethylbenzene in the complex, a small crystal was dissolved in cyclohexane and analyzed by FT-IR spectroscopy (IBM IR/85). The IR spectrum displayed only two peaks in the carbonyl region, at 1956.7 cm^{-1} (A_1) and 1883.4 cm^{-1} (E), indicating crystals of pure $(C_6(CH_3)_6)Cr(CO)_3$.

Data Collection.[15] A pale yellow prismatic crystal of $(C_6(CH_3)_6)Cr(CO)_3$ with approximate dimensions of 0.30 × 0.30 × 0.35 mm was selected for X-ray analysis. Data were collected on an Enraf-Nonius CAD-4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal, incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 23 reflections in the range $7° < \theta < 22°$ measured by the computer-controlled diagonal-slit method of centering. As a check on crystal quality, ω scans of several intense reflections were measured; the width at half height was 0.20° with a takeoff angle of 2.8°, indicating good crystal quality. The data were collected by using the ω–θ scan technique. The scan rate varied from 2 to 20°/min (in ω). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and ensures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ value of 60°. Equivalent reflections were collected. Below 2θ of 40°, four octants of data were collected. From 40 to 60° in 2θ, three octants of data were collected (except for $h > 10$, where only two were collected). The scan range (in degrees) was determined as a function of θ to correct for the separation of the Kα doublet; the scan width was calculated as follows: scan width = $(0.7 + 0.350 \tan \theta)°$.

A total of 9326 reflections were collected, of which 4024 were unique and not systematically absent. As a check on crystal stability, three representative reflections were measured every 33 min. The intensities of these standards remained constant, within experimental error, throughout data collection, so no decay correction was applied. Lorentz and polarization corrections were applied to the data. No absorption correction was made because of the small absorption coefficient (μ = 8.6 cm^{-1}) and the equidimensional nature of the crystal. A secondary extinction correction[16] was applied; the final coefficient, refined in least squares, was 0.000 000 5 (in absolute units). Intensities of equivalent reflections were averaged; 33 reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 7435 observed and accepted reflections were 2.3% on the basis of intensity and 1.8% on the basis of F_o. Table I summarizes the crystal parameters obtained in this study as well as the data measurement information.

Structure Solution and Refinement.[15] The structure was solved by using the Patterson heavy-atom method, which revealed the position of the Cr atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares where the function minimized was $\sum[w(|F_o|-|F_c|)^2]$ and the weight w is defined by $4(F_o)^2/\sigma^2(F_o^2)$. The standard deviation on σ/F^2) is derived from

$$\sigma^2(F_o^2) = [S^2(C + R^2B) + (P|F_o|^2)^2]/L_p^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, L_p is the Lorentz–polarization factor, and P is a factor introduced to downweight intense reflections, set to 0.050 in this study. Scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_c,[18] the values of df' and df'' were also taken from Cromer and Waber.[17] Only 2571 reflections with $I > 3\sigma(I)$ were used in the refinement, which involved 245 variable parameters. Following the initial refinement, a refinement using only high-angle data ($(\sin \theta)/\lambda > 0.55$ Å^{-1}) was carried out. The hydrogen atoms, scale factor, and extinction coefficient were fixed at values obtained from the full-angle refinement. The high-angle refinement involved 172 variables and 1076 observed data ($I > 3\sigma(I)$). Following the high-angle refinement a structure factor calculation was carried out on all observed data. The r values obtained were R_1 = 0.033 and R_2 = 0.053.

All calculations were performed in a PDP-11/73 based on the TEXRAY system, which includes the Enraf-Nonius SDP and proprietary crystallographic software of the Molecular Structure Corp.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. A-648) for the support of this work.

Supplementary Material Available: Tables of intermolecular contacts up to 3.75 Å and positional parameters, for the full data, bond lengths, bond angles, and general temperature factor expressions, for both high-angle data and full data, and least-squares planes and a stereoview of the unit cell (15 pages); a listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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(13) Byers, B. P.; Hall, M. B., submitted for publication in *Organometallics*.

(14) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

(15) The data were collected and the structure was solved by the Molecular Structure Corp.: M. W. Extine, P. N. Swepston, W. Pennington, J. M. Troup, and B. B. Warrington.

(16) Zachariasen, W. H. *Acta Crystallogr.* **1963**, 16, 1139.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV.

(18) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

Additions and Corrections

1986, Volume 25

Ch. Pulla Rao, J. R. Dorfman, and R. H. Holm*: Synthesis and Structural Systematics of Ethane-1,2-dithiolato Complexes.

Pages 428 and 430. In the abstract and in Table I the angle β for $(Et_4N)_2[Cd(edt)_2]$ should be 84.72 (2)°.—R. H. Holm