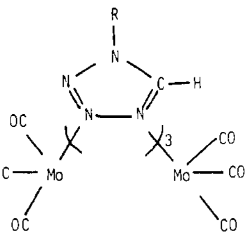

Figure 2. Proposed structure of tris[μ-(1-substituted tetrazole)]bis(tricarbonylmolybdenum).

the 1-PT complex, forming a pale yellow solution. The proton NMR of this solution is characteristic of uncomplexed 1-PT. The infrared spectrum of this solution shows peaks in the carbonyl region that are not assignable to Me$_2$SO at 1933 (w), 1901 (s), 1825 (m), 1783 (w), and 1753 cm^{-1} (br, s). These absorptions occur at lower energy than those observed for the 1-PT complex. In addition the chemistry is more complex than a simple substitution of 1-PT by Me$_2$SO to form only *fac*-Mo(CO)$_3$(Me$_2$SO)$_3$ since the infrared spectrum of this should exhibit only two absorptions assignable to CO. The character of this Me$_2$SO complex is not known at this time since all attempts to isolate a solid have proven unsuccessful.

All of these complexes as solids show some degree of air stability ranging from 2 h to several days for the 1-MT, 1-PT and 1-CT complexes, respectively. The increased stability can only be attributed to increased size of the tetrazole ring subsituents. Solutions of these complexes decompose when exposed to oxygen.

The solution infrared spectral results for the carbonyl region for the 1-CT and 1-MT complexes are indicative of a local C_{3v} symmetry for each molybdenum atom which, along with the observed stoichiometry of the complexes, suggests that each tetrazole is acting as a bridging bidentate ligand. A proposed structure that agrees with the rule of 18 and the stoichiometry is shown in Figure 2. If a C_{3v} symmetry is correct, the higher frequency carbonyl absorption is assigned as the A_1 mode, whereas the lower frequency is assigned as the E mode. The solution IR spectral results for the 1-PT complex and the solid-state forms for all complexes show more than two peaks. This can be interpreted if one assumes that the 1-PT complex and the solid-state complexes exist in more than one isomeric form with symmetries lower than C_{3v}. However the NMR spectrum for the 1-PT complex shows only one peak that can be assigned to the tetrazole ring C–H. Thus at least on the NMR time scale it is apparent that a C_3 axis is present.

Except for the tetrazole ring C–H stretch the remaining portions of the infrared spectra for these tetrazole complexes are quite similar to those observed for the uncomplexed ligands and shift only slightly upon complexation. The increase in the stretching energy upon complexation suggests that the hybrid orbital of carbon used in the formation of the C–H bond acquires more s character. This interpretation is consistent with the NMR observations, which indicate a slight deshielding of the ring C–H resonance upon complexation.

In the case of the 1-PT complex it is possible for the phenyl ring to form a η^6 complex with Mo. The NMR results indicate that this is certainly not the case since the phenyl multiplet is deshielded slightly upon complexation. In complexes such as η^6-C$_6$H$_6$Cr(CO)$_3$ the phenyl protons are shielded considerably as compared to those of the free ligand.[9]

The structure shown in Figure 2 suggests that N$_3$ and N$_4$ coordinate to the two molybdenum atoms. It is expected that the most basic tetrazole nitrogen would coordinate. The most basic nitrogen has been shown from ^{1}H and ^{13}C NMR studies of the protonation of 1-phenyltetrazole to be N$_4$.[10] This conclusion is supported in the crystal structure of dichlorobis(1-methyltetrazole)zinc(II),[2] where N$_4$ coordinates to zinc. In addition, since little difference is observed between those tetrazole complexes with a substituent with little steric factors (R = CH$_3$) and those with large steric factors (R = C$_6$H$_{11}$), the substituent most likely occupies that space that is in minimum contact with the carbonyl ligands. Such a situation would exist only if N$_3$ and N$_4$ coordinate as exhibited in Figure 2.

In summary the reaction between *fac*-tris(acetonitrile)molybdenum tricarbonyl and various 1-substituted tetrazoles resulted in the products (CO)$_3$Mo(1-RT)$_3$Mo(CO)$_3$ (R = CH$_3$, C$_6$H$_5$, C$_6$H$_{11}$). Elemental analyses and infrared and ^{1}H NMR spectral data indicate that the tetrazole ligand acts as an η^2 bridging ligand.

Acknowledgment. The author wishes to thank Indiana University, South Bend, IN, for partial support of this research through a Grant-in-Aid of Research and a Summer Faculty Fellowship.

Registry No. (CO)$_3$Mo(1-CT)$_3$Mo(CO)$_3$, 82150-32-1; (CO)$_3$Mo(1-PT)$_3$Mo(CO)$_3$, 82150-31-0; (CO)$_3$Mo(1-MT)$_3$Mo(CO)$_3$, 82150-30-9; Mo(CO)$_6$, 13939-06-5.

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[10] A. Könnecke, E. Lippman, and E. Kleinpeter, *Tetrahedron*, **33**, 1399 (1977).

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Electron Transfer. 56. Charge Effects in Inner-Sphere Reductions by Uranium(III)[1]

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Received February 24, 1982

A recent report[3] deals with pairs of (carboxylato)cobalt(III) complexes having similarly branched structures but differing in net charge. It was noted that inner-sphere chromium(II) reductions are more seriously retarded by incorporation of an additional positive center into the carboxyl group than are the corresponding reductions by vanadium(II) and europium(II). This difference was attributed to the mismatch of orbital symmetry between the acceptor π orbitals of the carboxyl bridge in the precursor complex and the migrating e_g electron of Cr^{2+}. A presumed consequence of such a mismatch is that electron transfer requires unsymmetric distortion of the ligand sheath about Cr^{II}, a distortion which is due in large part to water molecules in the second coordination sphere and which becomes less effective when alignment within this sphere is disrupted. An earlier communication[4] suggested that the migrating electron in 9-coordinate uranium(III) occupies an orbital having symmetry properties akin to those of the e_g orbital in Cr(H$_2$O)$_6$$^{2+}$, in keeping with the observation[4] that

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[2] On leave from Vivekananda College, Mylapore, Madras, India.

[3] Srinivasan, V. S.; Singh, A. N.; Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 1240.

[4] Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

Table I. Specific Rates for U^{3+} and $Ru(NH_3)_6{}^{2+}$ Reductions of (Carboxylato)pentaamminecobalt(III) Complexes[a]

oxidant	k_U[b]	k_{Ru}[c]
$[CH_3CH_2COO(Ro)]^{2+}$ (I)	5.3×10^3	0.030
$[NH_3CH_2COO(Ro)]^{3+}$ (II)	5.8×10^2	0.082[d]
$[(CH_3)_3CCH_2COO(Ro)]^{2+}$ (III)	1.01×10^3	0.023
$[(CH_3)_3NCH_2COO(Ro)]^{3+}$ (IV)	66	0.079
$[(CH_3)_3CCOO(Ro)]^{2+}$ (V)	42[e]	0.0087[f]
$[NH_3C(CH_3)_2COO(Ro)]^{3+}$ (VI)	5.1	0.061
$[C_6H_5CH_2COO(Ro)]^{2+}$ (VII)	3.1×10^3	0.027
$[1\text{-}pyCH_2COO(Ro)]^{3+}$ (VIII)	3.1×10^2	0.080
$[o\text{-}CH_3C_6H_4COO(Ro)]^{2+}$ (IX)	3.4×10^2	0.050
$[o\text{-}NH_3C_6H_4COO(Ro)]^{3+}$ (X)	28	0.058

[a] Specific rates are in $M^{-1}\ s^{-1}$. Ro = "roseo" = $(NH_3)_5Co^{III}$. [b] Reductions by U^{3+} were carried out in 0.20 M $HClO_4$ at 22 °C. [c] Reductions by $(NH_3)_6Ru^{2+}$ were carried out in 0.013 M HCl + 0.5 M LiCl at 25 °C. [d] Reference 3. [e] Reference 4. [f] Reference 5.

rates of inner-sphere reductions by U^{3+} exhibit a sensitivity to chain branching in the oxidant somewhat more marked than that found for Cr^{2+} reductions, the two reductants being, at the same time, much more selective than are V^{2+} and Eu^{2+}.

Extending this reasoning, one would expect rates of inner-sphere U^{3+} reductions to be perceptibly more responsive to charge variation in the oxidant than are reductions by Cr^{2+} and much more so than reductions by Eu^{2+} or V^{2+}. We find this to be the case.

Experimental Section

Materials. Solutions of $U(ClO_4)_3$ and $Ru(NH_3)_6Cl_2$ were prepared as described.[4,5]

Cobalt(III) complexes, listed in Table I, were available from a previous study.[3] Two series of carboxylato derivatives of $(NH_3)_5Co^{III}$ were used. The series featuring cations of 2+ charge was derived from acyclic or isocyclic acids; the remainder (3+ complexes) was derived from a group of betaines. Each member of the 2+ series is isosteric with a member of the 3+ series.

Rate Measurements. Rates were estimated from measurements of absorbance changes on a Cary Model 14 or Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer as described.[4,5] Reactions were first order each in Co^{III} and reductant but were carried out under nearly pseudo-first-order conditions. Most reductions were run with greater than a fivefold excess of reductant and were followed at 502 nm (the Co^{III} maximum). A few of the U^{3+} reductions were carried out with excess Co^{III} and more monitored at 350 nm (a U^{3+} maximum). The reaction medium for U^{III} reductions was 0.20 M $HClO_4$, whereas that for Ru^{II} reductions was 0.13 M HCl + 0.5 M LiCl + 0.1 M CH_3CN (the latter added as a scavenger for traces of $Ru(NH_3)_5H_2O^{2+}$ that may form during pretreatment of the Ru^{II} preparation).[6a] No systematic variation of the initial acidity was imposed; since the reagents used did not feature acidic centers having pK_A values in the range 1–3, rates were taken to be independent of acidity under the conditions used.[6b] Reactions were followed for at least 4 half-lives. Rate constants evaluated from successive half-life values within a single run, when adjusted for slight depletion of the reagent in excess, agreed to within 6%. No trends indicative of systematic errors were noted, and in cases where the ratio of reactants exceeded 10/1, average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs checked to better than 8%. Reductions by $Ru(NH_3)_6{}^{2+}$ were run at 25.0 ± 0.2 °C, whereas reactions of U^{3+} were carried out at 22.0 ± 0.5 °C.

Table II. Effect of Charge on Specific Rates of Reduction of Isosteric (Carboxylato)pentaamminecobalt(III) Derivatives[a]

	rel rates, 3+/2+ (obsd)				rel rates, 3+/2+ (IS calcd)[b]			
isosteres	Cr^{2+}	V^{2+}	Eu^{2+}	U^{3+}	Cr^{2+}	V^{2+}	Eu^{2+}	U^{3+}
II, I	0.37	0.77		0.11	0.36	0.75		0.11
IV, III	0.29	0.67	1.6	0.065	0.28	0.60	1.6	0.059
VI, V	0.47	0.63	1.1	0.12	0.39	0.55	1.1	0.090
VIII, VII	0.24	1.24	0.75	0.10	0.23	1.22	0.74	0.099
X, IX	0.10	0.61	0.58	0.082	0.093	0.60	0.58	0.079

[a] Individual specific rates, reaction conditions, and structural formulas of the oxidants are given in Table I and in ref 3. [b] Ratios of calculated inner-sphere components, obtained by subtracting the estimated outer-sphere components (see text) from the observed specific rates.

Results and Discussion

Specific rates for reductions by U^{3+} (k_U values) and by $Ru(NH_3)_6{}^{2+}$ (k_{Ru} values) are summarized in Table I. Oxidants are grouped into isosteric pairs with members of each pair differing in net charge. Comparison of rates within these pairs allows separation of charge effects from within these pairs allows separation of charge effects from steric influences. Note that in the case of $Ru(NH_3)_6{}^{2+}$, an outer-sphere reactant, the tripositive member of each oxidant pair reacts more rapidly than the dipositive despite the greater electrostatic barrier associated with the former. This doubtless reflects electron withdrawal (by the N^+ center) from Co^{III}, an effect which has been shown[5,7] to facilitate outer-sphere electron transfer.

With U^{3+}, as with Cr^{2+} and V^{2+}, each of which reacts predominantly by a bridged route in these systems, the 2+ oxidant is reduced at the greater specific rate. Rate ratios pertaining to each of the five isosteric pairs are listed in Table II for the various inner-sphere reductants. As predicted, selectivities for U^{3+} are more marked than those for Cr^{2+}, which are, in turn, more severe than those for Eu^{2+} or V^{2+}, in accord with differences in the symmetry characters of the donor orbitals.[4,5]

Measured specific rates are necessarily the sum of inner- and outer-sphere contributions. The latter are generally minor, but not necessarily negligible, and may be estimated from our k_{Ru} values by using proportionalities which have been shown to correlate outer-sphere specific rates for the various metal-center reductants.[5,8] Thus, it has been found that k_{Cr} values for a series of Co^{III} oxidants are very nearly $^1/_{100}$ of the corresponding k_{Ru} values[5] and that analogous proportionalities apply to outer-sphere rates by V^{2+}, Eu^{2+}, and U^{3+}, which are related to k_{Ru} by factors of $^1/_3$, $^1/_{10}$, and 22, respectively.[9,10] Subtraction of outer-sphere components, thus estimated, from the observed specific rates yields inner-sphere contributions, ratios of which are compared, on the right side of Table II, for the various isosteric pairs. In most cases, these ratios are very nearly the same as those for the composite rates, since

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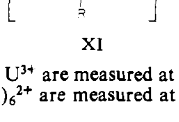
(5) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

(6) (a) We thank Professor H. Taube for suggesting this modification in procedure. (b) The initial value of $[H^+]$ (0.013 M), in the reductions by $Ru(NH_3)_6{}^{2+}$, was about 7 times the value of $[Co^{III}]_0$. Since every Co^{III} reduced releases five molecules of NH_3, $[H^+]$ dropped to less than 0.004 M during the course of each run. In no instance did distortion of the kinetic curve accompany this decrease in acidity.

(7) Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945.

(8) Proportionalities of this type are in accord with the Marcus model for outer-sphere reactions. See, for example: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(9) The k_U/k_{Ru} outer-sphere proportionality factor used here applies to reductions of carboxylato-bridged dimeric cobalt(III) complexes of type XI



XI

where specific rates with U^{3+} are measured at 21 °C in 0.25 M $HClO_4$ and those with $Ru(NH_3)_6{}^{2+}$ are measured at 25 °C in 0.5 M LiCl + 0.01 M HCl.[10]

(10) Srinivasan, V. S.; Singh, A. N.; Rajasekar, N.; Wieghardt, K.; Gould, E. S. *Inorg. Chem.*, in press.

only a small fraction of the entire reaction utilizes an outer-sphere path. Where differences exist, the trends have been somewhat sharpened. Adjustment for the outer-sphere components is most substantial in the case of the U^{3+} reduction of the α-aminoisobutyrato complex (VI), for which this treatment sets the inner-sphere specific rate as 3.9 M^{-1} s^{-1}. Here the combination of electrostatic and steric effects appears to have reduced the inner-sphere component to about 75% of the entire reaction.[11]

Registry No. I, 19173-62-7; II, 68582-30-9; III, 80327-80-6; IV, 45127-13-7; V, 33887-25-1; VI, 31133-42-3; VII, 40544-43-2; VIII, 69421-16-5; IX, 30931-78-3; X, 31133-44-5; $Ru(NH_3)_6^{2+}$, 19052-44-9; U, 7440-61-1; Cr, 7440-47-3; V, 7440-62-2; Eu, 7440-53-1.

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(11) A reviewer has pointed out that our argument may be strengthened by showing that the 3+/2+ outer-sphere ratio for each pair in Table II is greater than 1. Although we have not listed these ratios, the Ru^{II} data in Table I demonstrate that this is so since outer-sphere components of each reaction may be estimated by multiplying k_{Ru} by a constant characteristic of the reductant (as indicated in the text). Thus the calculated 3+/2+ outer-sphere ratio for each pair corresponds to the ratio of observed k_{Ru}'s; this ratio exceeds 1 in each case.

Communications

Characterization of a Mixed-Metal Bimetallic with an Unusual Set of Carbonyl Distortions: $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$

Sir:

Our recent disclosure of the synthesis[1] of $[Fe(CO)_4(SnR_2)]^{2-}$, coupled with a theoretical study[2] postulating an unusual $CO_{(eq)\pi^*}$ interaction, has suggested that careful study of other reduced mixed-metal bimetallic organometallic compounds may reveal subtle bonding patterns that may ultimately aid in the understanding of promotional effects induced by the M-L bond. We have examined the reduction of $[ZnFe(CO)_4]$ in Lewis bases yielding $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$. Its characterization and single-crystal X-ray diffraction structure determination serve as a basis for this report. The structure of the dianion (Figure 1) is highly novel as it represents an example of a zinc-capped iron tetrahedron that is intermediate between face capping and edge capping. Bonding in the dianion may be described as a near-ionic form. The sodium counterion has an unusual dimeric bridged structure.

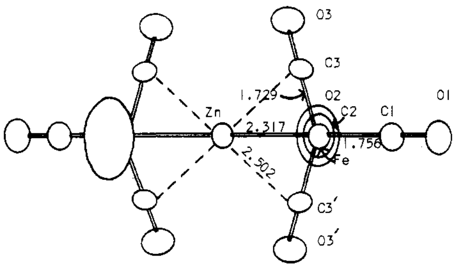

Figure 1. View of the $[Zn(Fe(CO)_4)_2]^{2-}$ anion. The Zn atom is located at a site of $2/m$ crystallographic symmetry with the Fe and carbonyl ligands CO(1) and CO(2) lying on the mirror plane. This results in overall C_{2h} symmetry for the ion.

The compound $[ZnFe(CO)_4]$, prepared in the form[3] $[(NH_3)_3ZnFe(CO)_4]$ (1.0 g, 3.53 mmol), was added to a solution of 1% Na/Hg amalgam in THF (50 mL) and stirred for $^1/_2$ h before being filtered through Celite to yield a yellow-orange solution of $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$. This complex may be isolated as very air-sensitive colorless crystals (0.82 g, 63%) with a light pink tint from a standing toluene/THF solution.[4] Crystals obtained from this solution were found to form in the monoclinic crystal system, space group *I*2/*m*, with two formula units per cell. The results of a molecular structure determination[5] show that the zinc atom is located at a site of $2/m$ symmetry with the iron atom and two carbonyl ligands of the independent $Fe(CO)_4$ fragment lying on a crystallographic mirror plane. A view of the $[Zn(Fe(CO)_4)_2]^{2-}$ anion is shown in Figure 1. The coordination geometry about the iron atoms resembles an intermediate case between a distorted tetrahedron with the Zn-Fe bond at an axial or face/edge capping site. A reasonable Fe-Zn single bond length, estimated from half the Fe-Fe length in $[Fe_2(CO)_8]^{2-}$ and the Zn-C length of $Zn(CH_3)_2$, would be approximately 2.56 Å.[6] This agrees well with an average value of 2.559 Å found[7] for $[(bpy)ZnFe(CO)_4]_2$ but is nearly 0.25 Å longer than the value of 2.317 (1) Å found for $[Zn(Fe(CO)_4)_2]^{2-}$. The sum of the zinc and carbon covalent radii is 2.08 Å, although zinc-carbon bond lengths in alkyl complexes are generally found to be less than 2.0 Å. The major distortion from a regular TBP geometry is found for the axial carbonyl ligand CO(1) and two equatorial carbonyl ligands CO(3) and CO(3′), which are bent toward the zinc atom. The trans Zn-Fe-C(1) angle was found to be 162.3 (2)° and the cis Zn-Fe-Cn(3) angle is 74.8°. The carbonyl carbon atom C(3) and the three symmetrically related carbonyl carbons form a square-planar geometry about the Zn with a Zn-C interatomic contact distance of 2.502 (5) Å. We have found in other studies a marked tendency for carbonyl ligands of complexes containing polar heterobimetallic metal-metal bonds to be oriented toward the M-M′ bond for either electronic or steric reasons.[8] Initial theoretical studies suggest little or no bonding of the $CO_\pi \rightarrow Zn_{p\pi}$ type. In the neutral cobalt analogue of the anion, $[Zn(Co(CO)_4)_2]$, the coordination spheres about the cobalt

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(1) Sosinsky, B. A.; Shelly, J.; Shong, R. *Inorg. Chem.* **1981**, *20*, 1370.

(2) Silvestre, J.; Albright, T. A.; Sosinsky, B. A. *Inorg. Chem.* **1981**, *20*, 3937.

(3) Hsieh, A. T. T.; Mays, M. J.; Platt, R. H. *J. Chem. Soc. A* **1971**, 3296. Hsieh, A. T. T.; Mays, M. J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *6*, 43.

(4) Data for the complex $[Na(THF)_2]^+{}_2[ZnFe(CO)_4)_2]^{2-}$: mp 175 °C (in vacuo); IR (KBr) 1990 (sh), 1952 (m), 1894 (w), 1809 (vs) cm^{-1}; IR (THF) 1990 (sh), 1970 (sh), 1941 (s), 1868 (vs), 1852 (vs), 1817 (vs) cm^{-1}; conductivity (CH_3CN) 463.18 Ω (mhos L cm^{-1} mol^{-1}) for mol wt 735.6; ^{57}Fe Mössbauer $\delta = 0.416$ mm/s, $\Delta = 1.429$ mm/s (relative to SNP). Anal. Calcd for $Na_2Fe_2ZnC_{24}H_{32}O_{12}$: C, 39.18; H, 4.35; Zn, 8.89; Fe, 15.18. Found: C, 39.35; H, 4.51; Zn, 8.52; Fe, 14.90.

(5) X-ray data for $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$: space group *I*2/*m*, monoclinic; 1092 unique reflections $[F_o^2 > 3\sigma(F_o^2)]$; $a = 10.654$ (3) Å, $b = 9.848$ (3) Å, $c = 15.333$ (3) Å, $\beta = 100.79$ (2)°, $V = 1580$ Å^3; $Z = 2$; $R_F = 0.048$, $R_{wF} = 0.057$; bond lengths Fe-Zn = 2.317 (1), Fe-C(1) = 1.756 (8), Fe-C(2) = 1.743 (9), Fe-C(3) = 1.729 (5), ZnC(3) = 2.502 (5), C(1)-O(1) = 1.147 (9), C(2)-O(2) = 1.128 (10), C(3)-O(3) = 1.172 (6), O(3)-Na = 2.308 (4), O(1)-Na = 2.584 (7) Å; bond angles Zn-Fe-C(1) = 162.3 (2), Zn-Fe-C(2) = 90.5 (3), Zn-Fe-C(3) = 74.8 (1), C(1)-Fe-C(2) = 107.2 (4), C(1)-Fe-C(3) = 98.2 (2), C(2)-Fe-C(3) = 110.8 (2), C(3)-Fe-C(3)′ = 127.9 (3), Fe-C(1)-O(1) = 177.5 (7), Fe-C(2)-O(2) = 178.9(9), Fe-C(3)-O(3) = 177.7 (7), C(3)-Zn-C(3)′ = 76.7 (2)°.

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