Table VI. Spectral Data and Conductance Measurements[a]

	λ_{max}, cm^{-1} (ϵ_{max}, M^{-1} cm^{-1})		
	ν_2	ν_3	Λ_M,[b] Ω^{-1} cm^2 mol^{-1}
solid	17857	28329 sh	
H_2O	15503 (6)	26315 sh	213
DMSO	15673 (7)	26315 sh	26
DMF	15389 (11)	25000 sh	21

[a] sh = shoulder. [b] At 298 K.

shown in Table V. Since in the title compound there are several C—N and N—H groups (from the Acm and from the ammonia) the correspondent IR bands do not give information about which groups have been modified. The first significant difference between the IR spectrum of the present complex and those of the previously cited complexes concerns the splitting of the absorption frequencies of the carbonyl group. While the Zn and Co complexes present a very strong band at higher frequencies than in Acm, the Ni complex shows a very weak band at 1681 cm^{-1} and a medium one at 1624 cm^{-1}. This is a consequence of the deprotonation of the acetamido group, resulting in a delocalization of the negative charge on the carbonyl double bond by way of several resonance forms and leading to a great reduction of the C=O bond order. The longer C=O bond length and the shorter C—N bond length of the acetamido group in the complex compared with the same bond length in the Acm structure are in agreement with the IR results.

Although from the IR data it could be inferred that the coordination takes place through the carbonyl group, the crystal structure shows that the change in this stretching vibration is due to the deprotonation. On the other hand, the asymmetric and symmetric stretching vibrations of the SO_2 group have not changed in comparison to those of the free ligand. This indicates that there is no interaction between the sulfonamido group and the metal ion, which is also confirmed by the X-ray analysis. In the Zn and Co complexes, this bands are shifted to lower frequencies, suggesting a different mode of coordination, which the sulfonamido group is involved in.

From the crystal structure of the Ni complex it could be said that the more acidic proton of the Acm is the amido one; however, the behavior of that ligand does not have to be similar in complexes with other ions. So, in the Zn and Co complexes the spectroscopic data evidence that deprotonation takes place in the sulfonamido group. In addition, the crystal structure of a Cu(II) complex, which will be reported later, shows the ligand with a double deprotonation.

The solid d–d spectrum shows three characteristic bands of Ni(II) in an octahedral environment. The *B* and 10*Dq* values (1080 and 10840 cm^{-1}, respectively) fall within the range observed for a NiN_6 chromophore.[12] The room-temperature magnetic moment calculated by the Faraday method (3.21 μ_B) represents the usual behavior for a mononuclear and distorted octahedral Ni(II) complex. The reflectance spectrum and the magnetic data are in agreement with the X-ray results.

The solid compound and its aqueous, dimethyl sulfoxide, and *N,N'*-dimethylformamide solutions have different colors and electronic spectra, and thus, we would expect a different chromophore. Nevertheless, the spectral data (see Table VI) indicate an octahedral environment. These results and the conductance measurements suggest that solvent molecules replace the ligand in the Ni(II) coordination sphere.

Acknowledgment. We greatly appreciate financial support from the Comisión Asesora de Investigación Científica y Técnica, Spain (Grant 932/84).

Supplementary Material Available: Tables of equations of least-squares planes, fractional coordinates for hydrogen atoms, and anisotropic thermal parameters (3 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Lewis Base Adducts of Main Group 1 Metal Compounds. 7.† The Lithium–Coinage-Metal Parallel: Novel Adducts of Lithium(I) Bromide and Iodide with 2,6-Dimethylpyridine

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Copper(I) halides, CuX (X = Cl, Br, I), with monodentate nitrogen bases, L, yield adducts of stoichiometry $XCuL_n$, chiefly for n = 1–3, exhibiting a variety of oligomeric and polymeric forms,[2] over which some control may be exercised by the stoichiometry of the reaction conditions and the steric profile of the ligand. With silver(I),[3] as the consequence of a change in balance between solvation and lattice energies, the higher values of n become much more difficult to access, while the isomeric possibilities found in the copper system are much more restricted but with new forms emerging, as the consequence of both energetic considerations and the larger size of silver(I). In this context, our recent studies with lithium(I),[4,5] demonstrating, perhaps surprisingly, characteristics with respect to complex formation intermediate between those of copper(I) and silver(I) by virtue of the formation of species of high n, but with a metal radius nearer that of silver(I), emerge with considerable novelty. Recrystallization of the lithium halides from 3,5-dimethylpyridine (3,5-dmpy) yields the mononuclear series of four-coordinate species $[XLiL_3]$[5,6] paralleling the previously characterized copper(I) series, while similar parallel series are found with 2-methylpyridine (2-mpy) as the binuclear arrays $L_2MX_2ML_2$ (M = Cu,[7] Li;[5] X = all Cl, Br, I). With 2,6-dimethylpyridine (2,6-dmpy), recrystallization of CuX yields mononuclear, three-coordinate L_2CuX.[8,9]

Recrystallization of the copper(I) halides from the parent base is usually readily accomplished, providing air is excluded; with lithium the (more difficult) problem is the total exclusion of moisture, and we find the formation of crystalline lithium(I) halide–nitrogen base adducts a more difficult procedure. In attempting the synthesis of adducts with 2,6-dmpy, we have thus far achieved success only with the bromide and iodide, obtaining complexes characterized by analysis and single-crystal structure determination as 1:1.5 and 1:2 species, respectively.

The iodide is a 1:2 complex, but, unlike its copper(I) counterpart,[8] it is a binuclear, centrosymmetric $L_2LiI_2LiL_2$ species, the first binuclear species of this type obtained with this ligand, presumably a consequence of the increased size of lithium(I) vs that of copper(I). (Note, however, that the relation is not simple: in $[(3,5\text{-dmpy})_3MX]$, for X = Cl, Br, I, M–X distances are 2.320 (9), 2.51 (2), and 2.80 (1) Å for M = Li[4] and 2.412 (9), 2.51 (1), and 2.683 (3) Å for M = Cu[6]). Geometries of the $N_2LiI_2LiN_2$ (L = 2-mpy,[5] 2,6-dmpy) and $N_2CuI_2CuN_2$ (L = 2-mpy[7]) systems are compared in Table II. We note the generally increased Li–N and Li–I distances in the 2,6-dmpy complex, and in this complex the I–M–N angles are divided into two sets, ca. 95 and 134°, suggestive of the presence of steric strain in the 2,6-dmpy adduct, as might be expected. The ligand disposition may be compared with that of unstrained $[(3,5\text{-dmpy})_2CuI_2Cu(3,5\text{-dmpy})_2]$,[8] which adopts almost perfect *mmm* symmetry. With 2,6-substituents maximum symmetry may be achieved by cleavage of the dimer to a monomer with concomitant opening of the N–Cu–N ring angle to ca. 150°—this disposition with incipient 2*mm* symmetry is found in both forms of $[(2,6\text{-dmpy})_2CuI]$.[8] Alternatively, the dimer may be preserved with loss of symmetry to diminish interactions between the methyl groups on ligands *gem* to the same metal; this is achieved by a twist of the N_2M planes about the M···M axis so that they no longer lie normal to the MX_2M plane.

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† Part 6: Raston, C. L.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 413.

Table I. Crystallographic data for $Li_4Br_4L_6$ and $Li_2I_2L_4$, L = 2,6-Dimethylpyridine

	(a) $Li_4Br_4L_6$
$C_{42}H_{54}Br_4Li_4N_6$	$M_r = 990.3$
$a = 13.020$ (8) Å	triclinic, space group $P\bar{1}$ (No. 2)
$b = 12.191$ (9) Å	$T = 22$ °C
$c = 8.265$ (4) Å	$\lambda = 0.71069$ Å
$\alpha = 93.94$ (4)°	$\rho_{calcd} = 1.42$ g·cm^{-3}
$\beta = 102.68$ (4)°	$\mu = 34.5$ cm^{-1}
$\gamma = 113.23$ (5)°	$A^* = 2.2$–3.7
$V = 1158$ (1) Å^3	$R(F_o) = 0.048$
$Z = 1$	$R'(F_o) = 0.054$
	(b) $Li_2I_2L_4$
$C_{28}H_{36}I_2Li_2N_4$	$M_r = 696.3$
$a = 11.022$ (5) Å	triclinic, space group $P\bar{1}$ (No. 2)
$b = 10.024$ (5) Å	$T = 22$ °C
$c = 8.352$ (3) Å	$\lambda = 0.71069$ Å
$\alpha = 69.36$ (3)°	$\rho_{calcd} = 1.42$ g·cm^{-3}
$\beta = 79.90$ (3)°	$\mu = 18.4$ cm^{-1}
$\gamma = 70.76$ (3)°	$R(F_o) = 0.029$
$V = 813.5$ (6) Å^3	$R'(F_o) = 0.028$
$Z = 1$	

Table II. $N_2MI_2MN_2$ Core Parameters (L = Ligand)

	M = Li, L = 2,6-dmpy[a]	M = Li, L = 2-mpy[b]	M = Cu, L = 2-mpy[c]
	Distances (Å)		
M–N(1)	2.123 (9)	2.08 (1)	2.05 (1)
M–N(2)	2.135 (9)	2.09 (1)	2.06 (1)
M–I	2.932 (6)	2.821 (10)	2.714 (3)
M–I′	2.913 (7)	2.768 (9)	2.663 (3)
M···M	3.971 (15)	3.589 (12)	3.083 (3)
I···I	4.270 (1)	4.285 (2)	4.407 (3)
	Angles (deg)		
M–I–M	86.2 (2)	79.9 (3)	69.95 (6)
I–M–I′	93.8 (2)	100.1 (3)	110.05 (6)
I–M–N(1)	94.8 (2)	111.2 (5)	107.9 (3)
I–M–N(2)	135.0 (3)	110.7 (4)	106.5 (3)
I′–M–N(1)	133.0 (3)	113.5 (5)	104.6 (3)
I′–M–N(2)	95.6 (3)	111.9 (5)	109.7 (4)
N–M–N	109.9 (3)	109.2 (4)	117.9 (2)
	Plane Deviations (Å)		
δ(M)[d]	0.074	0.108	0.065
	0.266	0.218	0.123
δ(N(1))[e]	0.859	1.676	1.786
δ(N(2))	−1.483	−1.720	−1.730

[a] This work. [b] Reference 5. [c] Reference 7. [d] Deviation of M from ligand plane. [e] Deviation of N from MI_2M plane.

Interestingly, in the present compound the twists of the two N_2M planes about this axis are concerted and associated further with twists of the ligands about the Li–N bonds so that the methyl groups from either end of the molecule are brought into proximity, the incipient symmetry of the dimer becoming *2/m*. A final point of interest is the very large Li···Li distances observed in the dimeric lithium halide adducts, in comparison to the Cu···Cu distances found in the present compound and related systems.

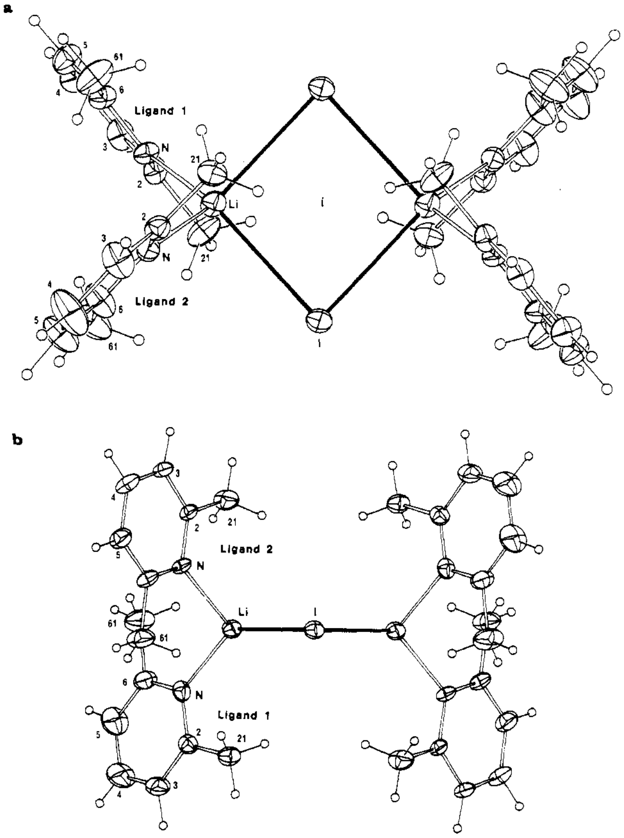

Figure 1. The 1:2 lithium iodide–2,6-dmpy dimer projected (a) normal to the Li_2I_2 plane and (b) along the line in that plane normal to the Li···Li vector. In Figures 1 and 2, 20% probability amplitude thermal ellipsoids are shown, together with the non-hydrogen atom-numbering system. Hydrogen atoms have arbitrary radii of 0.1 Å.

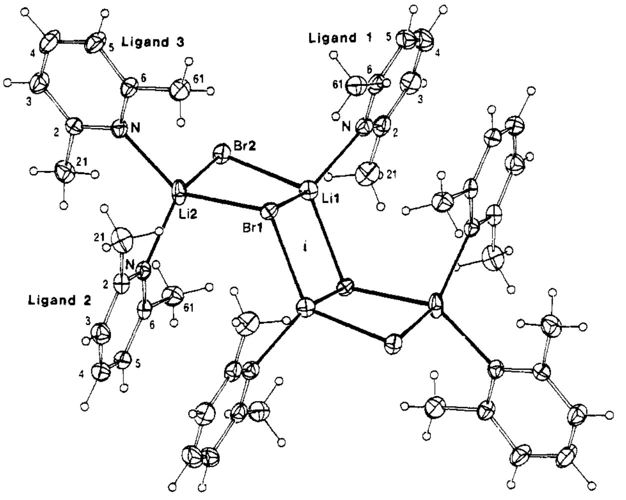

Figure 2. The 1:1.5 lithium bromide–2,6-dmpy tetramer.

The bromide is a 1:1.5 complex. This stoichiometry is well-known among copper(I) halide–triphenylphosphine adducts, where the form adopted is that of a dimer, $LCuX_2CuL_2$, containing three- and four-coordinate copper(I).[10] With nitrogen bases, only one example of this stoichiometry has been recorded, adopting a "step" tetranuclear structure.[11] With triphenylphosphine adducts of the coinage-metal(I) halides, the "step" tetramer is well-known[12] in systems of 1:1 stoichiometry as the alternative to the "cubane"

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Table III. "Step-Structure" Parameters

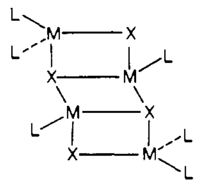
	$[Li_4Br_4(2,6\text{-dmpy})_6]$[a]	$[Cu_4I_4(2\text{-mpy})_6]$[b]
	Distances (Å)	
M(1)–X(1)	2.65 (2)	2.719 (2)
M(1)–X(1′)	2.54 (1)	2.721 (2)
M(1)–X(2)	2.56 (1)	2.661 (2)
M(2)–X(2)	2.54 (2)	2.694 (2)
M(2)–X(1)	2.66 (1)	2.713 (2)
M(1)···M(1′)	3.59 (2)	3.459 (2)
X(1)···X(1′)	3.751 (2)	4.199 (3)
M(1)···M(2)	3.39 (2)	3.012 (2)
X(1)···X(2)	3.913 (3)	4.462 (3)
M(1)–N(1)	2.15 (2)	2.045 (5)
M(2)–N(2)	2.19 (1)	2.050 (4)
M(2)–N(3)	2.14 (2)	2.059 (5)
	Angles (deg)	
N(1)–M(1)–X(1)	128.1 (7)	106.8 (2)
N(1)–M(1)–X(1′)	114.7 (7)	118.1 (1)
N(1)–M(1)–X(2)	99.8 (5)	115.1 (1)
X(1)–M(1)–X(1′)	92.5 (5)	101.04 (4)
X(1)–M(1)–X(2)	97.4 (5)	112.07 (6)
X(1′)–M(1)–X(2)	126.1 (6)	103.02 (4)
M(1)–X(1)–M(1′)	87.5 (5)	78.97 (4)
M(1)–X(1)–M(2)	79.4 (5)	67.34 (4)
M(1′)–X(1)–M(2)	114.3 (4)	109.35 (3)
M(1)–X(2)–M(2)	83.4 (5)	68.46 (5)
X(1)–M(2)–X(2)	97.5 (5)	111.23 (5)
X(1)–M(2)–N(2)	127.6 (7)	108.5 (1)
X(1)–M(2)–N(3)	96.3 (5)	98.5 (1)
X(2)–M(2)–N(2)	98.8 (5)	103.9 (2)
X(2)–M(2)–N(3)	130.2 (8)	109.7 (2)
N(2)–M(2)–N(3)	109.6 (7)	124.9 (2)

[a]This work; X = Br. [b]Reference 11; X = I.

Table IV. Non-Hydrogen Atom Coordinates (Iodide)

atom	*x*	*y*	*z*
I	0.12794 (3)	1.10595 (3)	0.31609 (4)
Li	0.1487 (7)	0.8252 (7)	0.5975 (9)
N(11)	0.3034 (3)	0.8383 (4)	0.7054 (4)
C(12)	0.2785 (4)	0.8973 (4)	0.8328 (5)
C(121)	0.1437 (4)	0.9476 (5)	0.8955 (6)
C(13)	0.3762 (5)	0.9137 (6)	0.9040 (7)
C(14)	0.5002 (5)	0.8713 (8)	0.8362 (10)
C(15)	0.5256 (5)	0.8130 (7)	0.7033 (9)
C(16)	0.4248 (5)	0.7976 (6)	0.6424 (7)
C(161)	0.4486 (5)	0.7336 (8)	0.4969 (8)
N(21)	0.1756 (3)	0.5998 (3)	0.6145 (4)
C(22)	0.1708 (4)	0.5666 (4)	0.4742 (5)
C(221)	0.1667 (5)	0.6876 (5)	0.3070 (6)
C(23)	0.1703 (4)	0.4282 (5)	0.4803 (6)
C(24)	0.1768 (5)	0.3186 (5)	0.6359 (7)
C(25)	0.1807 (5)	0.3507 (5)	0.7797 (6)
C(26)	0.1803 (4)	0.4915 (5)	0.7657 (6)
C(261)	0.1819 (6)	0.5319 (6)	0.9223 (6)

form. With two of the metal atoms three-coordinate at the periphery it offers a sterically less crowded alternative; with the nitrogen base example $[Cu_4I_4(2\text{-mpy})_6]$,[11] the additional pair of ligands are employed in increasing the coordination number of the peripheral metal sites to 4 also. The overall structure is



The present lithium bromide–2,6-dmpy adduct is, surprisingly, an example of this unusual form and is compared with $[Cu_4I_4(2\text{-mpy})_6]$ in Table III. Less surprising, perhaps, is the observation that the angular geometries of the two systems differ considerably, a consequence of many differences in the basic parameters of the two systems: metal, halide, and ligand profile. As for the 2-mpy–copper(I) iodide adduct, the tetramer is centrosymmetric.

Table V. Non-Hydrogen Atom Coordinates (Bromide)

atom	*x*	*y*	*z*
Br(1)	−0.12629 (7)	−0.02055 (7)	0.58786 (10)
Br(2)	−0.20578 (7)	−0.32571 (7)	0.29760 (11)
Li(1)	−0.025 (1)	−0.156 (1)	0.497 (2)
Li(2)	−0.295 (1)	−0.177 (1)	0.331 (2)
N(11)	0.0440 (6)	−0.2621 (6)	0.6459 (9)
C(12)	0.0992 (7)	−0.3177 (7)	0.5795 (12)
C(121)	0.1229 (9)	−0.2876 (8)	0.4151 (14)
C(13)	0.1304 (8)	−0.4018 (8)	0.6536 (15)
C(14)	0.1070 (9)	−0.4273 (8)	0.8036 (15)
C(15)	0.0511 (8)	−0.3719 (8)	0.8764 (12)
C(16)	0.0206 (7)	−0.2895 (7)	0.7924 (12)
C(161)	−0.0406 (8)	−0.2273 (8)	0.8640 (12)
N(21)	−0.3105 (5)	−0.0452 (5)	0.1811 (8)
C(22)	−0.3642 (7)	0.0241 (7)	0.2169 (10)
C(221)	−0.4136 (9)	0.0035 (9)	0.3628 (12)
C(23)	−0.3697 (8)	0.1133 (8)	0.1280 (12)
C(24)	−0.3227 (8)	0.1300 (8)	−0.0058 (13)
C(25)	−0.2690 (7)	0.0600 (7)	−0.0457 (10)
C(26)	−0.2621 (7)	−0.0251 (7)	0.0521 (10)
C(261)	−0.1958 (8)	−0.0960 (8)	0.0228 (11)
N(31)	−0.4684 (5)	−0.3058 (5)	0.3352 (8)
C(32)	−0.5463 (7)	−0.3753 (7)	0.1913 (10)
C(321)	−0.5134 (8)	−0.3506 (8)	0.0318 (11)
C(33)	−0.6506 (8)	−0.4678 (8)	0.1916 (12)
C(34)	−0.6769 (8)	−0.4892 (9)	0.3397 (15)
C(35)	−0.5993 (8)	−0.4208 (9)	0.4887 (12)
C(36)	−0.4956 (7)	−0.3277 (7)	0.4806 (11)
C(361)	−0.4076 (8)	−0.2521 (9)	0.6389 (11)

Experimental Section

Synthesis. 2,6-dmpy was dried over sodium pieces for 1 h prior to use, filtered, and vacuum–freeze degassed. A mixture of excess lithium halide, previously dried at 180 °C under vacuum for 1 day, and 10–30 mL of ligand was refluxed for several minutes and the solution filtered while hot under argon and allowed to cool slowly in a Dewar flask filled with boiling water. Substantial crystals were obtained in both cases.

The lithium bromide–1.5(2,6-dmpy) adduct, like many other derivatives of this type, does not exhibit a single sharp melting point when heated in a sealed capillary. In the present case a phase change was observed at 54 °C, followed by melting at 116–120 °C and decomposition at 150 °C, presumably corresponding to phases with a lower LiBr:2,6-dmpy ratio. The 1:2 iodide adduct exhibited a phase change at 66 °C, melting at 129–130 °C. Satisfactory analyses were obtained for both species. Anal. Calcd for $C_{21}H_{27}Br_2Li_2N_3$: C, 50.9; H, 5.5; N, 8.5. Found: C, 50.1; H, 5.4; N, 8.3. Calcd for $C_{14}H_{18}ILiN_2$: C, 48.3; H, 5.2; N, 8.1. Found: C, 47.5; H, 5.2; N, 7.8.

Structure Determination. Specimens for the crystallographic work were mounted in capillaries. Unique data sets were measured within $2\theta_{max}$ limits of 45° (bromide) and 50° (iodide), with use of a Syntex $P2_1$ four-circle diffractometer fitted with a monochromatic Mo Kα radiation source and operating in conventional $2\theta/\theta$ scan mode; 3623 and 2842 independent reflections for bromide and iodide respectively were measured, 2494 and 2353 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after analytical absorption correction (bromide only) (crystal dimensions 0.30 × 0.36 × 0.50 mm (bromide), ~0.40 × 0.30 × 0.40 mm irregular fragment (iodide)) and solution of the structure by vector methods (function minimized $\sum w\Delta|F|^2$; number of variables 253 (bromide), 163 (iodide)). Anisotropic thermal parameters were refined for the non-hydrogen atoms; x, y, z, and U_{iso} values for hydrogen were included constrained at estimated values. At convergence, residuals on $|F|$ were conventional R, R' statistical weights, derivatives of $\sigma^2(I) = \sigma^2(I_{diff}) + 10^{-4}n_w\sigma^4(I_{diff})$ (n_w = 4 (bromide), 1 (iodide)) being employed. Neutral-atom complex scattering factors were employed;[13] computation used the XTAL 83 program system[14] implemented on a Perkin-Elmer 3240 computer.

Registry No. $Li_4Br_4L_6$, 117687-79-3; $Li_2I_2L_4$, 117687-80-6.

Supplementary Material Available: Tables SUP-1–6, giving thermal and hydrogen atom parameters and ligand non-hydrogen geometries (6 pages); tables of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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