A comparison of the (–Mn(III)–N–O–)$_4$ core with that of the crown ethers is interesting. The bite distance[5,7] and cavity size[5,7] for 12-crown-4 (2.79 and 0.6 Å) is similar to **1** where the average bite distance is 2.67 Å and the cavity size is 0.5 Å. One might expect an expansion of the cavity of the 12-$\mathrm{C}_{\mathrm{Mn}^{3+}\mathrm{N}}$-4[8] compared to 12-crown-4 as a result of the increased Mn–N ($\mathrm{av}_{\mathrm{ring}}$ = 1.97 Å; range = 1.93–1.99) and Mn–O ($\mathrm{av}_{\mathrm{ring}}$ = 1.87 Å; (1.83–1.88 Å)) distances relative to the corresponding C–C (1.50 Å) and C–O (1.42 Å) distances. However, this bond distance increase is compensated by the bond angles about the Mn(III) ion. In the crown complexes[1-5,7,9,10] angles between 108° and 113° are commonplace, while the average O–Mn–N, Mn–N–O, and N–O–Mn angles are 88° (87–89), 119° (117–121), and 116° (114–117), respectively. Thus, the octahedral angle decreases the cavity size even though the Mn(III)–O and Mn(III)–N distances have been elongated. We have shown[11] that SHI will form a stable trinuclear oxovanadium(V) cluster **2**, [VO(salicylhydroximate)($\mathrm{CH_3OH}$)]$_3$. The central core of this molecule is composed of (–M–N–O–)$_3$ linkages, making this compound analogous to 9-crown-3 (9-$\mathrm{C}_{\mathrm{V}^{5+}\mathrm{N}}$-3). The cavity sizes of both 9-crown-3 and 9-$\mathrm{C}_{\mathrm{V}^{5+}\mathrm{N}}$-3 are too small to accommodate other ions. Therefore, unlike **1**, the hydroxylimino oxygens of **2** were coordinated solely to the vanadium(V).

On the basis of solution conductivity, ^{1}H NMR, and EPR measurements,[12] the cluster **1** completely dissociates when dissolved in methanol. Although poorly soluble, the complex appears to retain its integrity as a pentanuclear cluster in acetonitrile. An intermediate behavior is observed in DMF where 20% of the Mn(II) dissociates from the cluster; however, the [Mn(SHI)]$_4$ core remains intact.[12] This solution chemistry is similar to that reported for **2** which is very stable in acetonitrile but dissociates in methanol. The room temperature, solid-state susceptibility of **1** (13.8 μ_B/cluster) is greater than the predicted spin only moment (11.4 μ_B/cluster) indicating that the compound is weakly ferromagnet. Variable temperature measurements are in progress to ascertain the magnitude of the exchange coupling in this material.

In conclusion, the first example of a crown ether type coordination mode using a ring system composed partially of transition-metal ions and entirely of heteroatoms has been achieved by stabilizing a cluster of manganese with a high denticity ligand that has the capacity to form M–N–O–M linkages. This unique example of metal ion recognition illustrates a possible direction for designing moderate nuclearity clusters which, through the judicious choice of the capping metal ion, may have interesting magnetic and spectroscopic properties.

Acknowledgment. We acknowledge financial support from NIH Grant GM-39406, and V.L.P. thanks the G. D. Searle Family/Chicago Community Trust for a Biomedical Research Scholars Award (1986–1989) and The Alfred P. Sloan Foundation for a Sloan Fellowship (1989–1991).

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Supplementary Material Available: Table I, fractional atomic coordinates for all atoms; Table II, thermal parameters for all atoms; Table III, bond distances for all atoms; Table IV, bond angles for all atoms; and Figure 3, {$\mathrm{Mn^{II}[Mn^{III}}$(salicylhydroximate)]$_4$(acetate)$_2(DMF)_6$}·2DMF, showing the complete atom numbering scheme (25 pages); Table V, observed and calculated structures factors (16 pages). Ordering information is given on any current masthead page.

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[7] Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271. *Synthetic Multidentate Macrocyclic Compounds*; Izatt, R., Christensen, J. J., Eds.; Academic Press: New York, 1978.

[8] Our proposed nomenclature is *X*-$\mathrm{C}_{\mathrm{M}^{n+}\mathrm{H}}$-*Y* where X and Y indicate ring size and oxygen donor atoms, M and n are the metal and its oxidation state, and H is the identity of the remaining heteroatom bridge. Thus, 12-$\mathrm{C}_{\mathrm{Mn}^{3+}\mathrm{N}}$-4 indicates the basic core structure of 12-crown-4 with the carbon atoms replaced by Mn(III) and N atoms throughout the ring. A similar situation is described by the vanadium(V) analogue 9-$\mathrm{C}_{\mathrm{V}^{5+}\mathrm{N}}$-3.

[9] Seiler, P.; Dobler, M.; Dunitz, J. D. *Acta Crystallogr.* **1974**, *B30*, 2744.

[10] Mason, E.; Eick, H. A. *Acta Crystallogr.* **1982**, *B38*, 1821.

[11] Pecoraro, V. L. *Inorg. Chim. Acta* **1989**, *155*, 171.

[12] The X-band EPR spectrum of **1** in methanol at 110 K shows a very strong six-line component that is the hallmark of uncomplexed Mn(II). In DMF, a six-line signal is also observed; however, a standard curve indicates that this signal arises from 20 ± 10% of the Mn(II) in the sample. Addition of methanol to this DMF solution causes a dramatic increase in the six-line signal. In contrast, acetonitrile solutions of **1** contain an additional broad derivative shaped resonance centered at $g = 2$ that underlies a very weak six-line signal. The intensity of this broad feature is slightly greater at 4 K than at 110 K suggesting that it arises from the electronic ground state. Thus, we believe that this poorly resolved signal is associated with the intact cluster, while the small amount of six-line signal corresponds to less than 5% of the overall spin. These conclusions are supported by the ^{1}H NMR of **1** in different solvents. No paramagnetically shifted resonances are seen in methanol-d_4 showing that the entire complex has dissociated. In DMF-d_6, coordinated acetate resonances are observed at +56.1 ppm, and resonances from the phenolate ring protons are at –14.1, –15.5, –22.4, and –23.0 ppm. The same peaks are observed at –16.4, –17.6, –21.4 and –22.0 ppm (phenolate) and +60.6 ppm (acetate) in acetonitrile-d_3. The acetate resonances were confirmed by obtaining spectra of **1** prepared using acetate-d_3.

Evidence for Positive Hole Delocalization over Two Double Bonds Separated by 6 Å in the Cation Radical of a Nonconjugated Diene: A Consequence of Laticyclic Hyperconjugation

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Recent photoelectron spectroscopic (pes) studies on the dienes **1a**[1] and **2**[2] and their dibenzo analogues[2] revealed the presence of unusually large π,π splittings which were attributed to a novel variant of through-bond interactions,[3] called laticyclic hyperconjugation.[1b,4] In this model, interactions occur through the mixing of the π orbitals of **1a** and **2** with the pseudo-π orbital(s) of the central $\mathrm{CH_2}$ group(s), the overall interacting ribbon topology resembling the Goldstein–Hoffmann laticyclic array.[5] Thus, for **1a**, such mixing causes the b_1 $\pi_-(\equiv\pi-\pi)$ combination of π orbitals to be raised in energy, relative to the $a_1\pi_+(\equiv\pi+\pi)$ combination which, by dint of symmetry, cannot mix with the pseudo-π orbital of the $\mathrm{CH_2}$ group and whose energy, therefore, remains unchanged. The large degree of π,pseudo-π mixing can be seen from inspection of the atomic orbital coefficients in the (STO-3G) HOMO of the model ethene···$\mathrm{CH_4}$···ethene "complex" **4**, whose geometry mimics the orientation of the interacting components of **1a**.[3]

In view of the nexus between the rate of positive hole transfer in the ground-state cation radical of, say, a diene and the observed π,π splitting energy,[3d,6] the very large π,π splitting found for **1a** (0.52 eV[1a,b]) suggests that the rate of hole transfer between the two double bonds in the cation radical **1a**$^+$ could so fast (>10^{14}

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[1] (a) Jørgensen, F. S.; Paddon-Row, M. N.; Patney, H. K. *J. Chem. Soc., Chem. Commun.* **1983**, 573. (b) Jørgensen, F. S.; Paddon-Row, M. N. *Tetrahedron Lett.* **1983**, 5415. (c) Paddon-Row, M. N.; Englehardt, L. M.; Skelton, B. W.; White, A. H.; Jørgensen, F. S.; Patney, H. K. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1835. (d) Paddon-Row, M. N.; Cotsaris, E.; Patney, H. K. *Tetrahedron* **1986**, *42*, 1779.

[2] (a) Paddon-Row, M. N.; Patney, H. K.; Peel, J. B.; Willett, G. D. *J. Chem. Soc., Chem. Commun.* **1984**, 564. (b) Hush, N. S.; Willett, G. D.; Paddon-Row, M. N.; Patney, H. K.; Peel, J. B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 827. (c) Craig, D. C.; Paddon-Row, M. N.; Patney, H. K. *Aust. J. Chem.* **1986**, *39*, 1587.

[3] (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. (d) Paddon-Row, M. N.; Jordan, K. D. *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, NY, 1988; Chapter 3.

[4] Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 2* **1985**, 257.

[5] Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193.

[6] (a) Balaji, V.; Ng, L.; Jordan, K. D.; Paddon-Row, M. N.; Patney, H. K. *J. Am. Chem. Soc.* **1987**, *109*, 6957. (b) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

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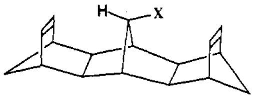
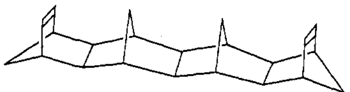


1a X = H
1b X = D



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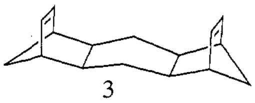

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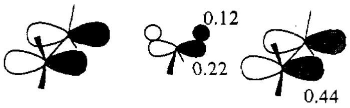

4

s^{-1}) that the hole is effectively delocalized over a symmetrical (C_{2v}) structure. We now present evidence to show that this may well be the case.

Exposure of a dilute (1:1000) solution of **1a** in $CF_2ClCFCl_2$ at 77 K to ^{60}Co γ rays gave a species, believed to be **1a**$^+$, whose ESR spectrum showed a symmetrical triplet with a hyperfine splitting (hfs) of 30 ± 2 G (Figure 1A). On the other hand, generation of the cation radical of **1b**$^+$,[7] the monodeuterated analogue of **1a**$^+$,[8] gave an ESR spectrum that showed a doublet with an hfs value (31 ± 2 G) identical with that observed for **1a**$^+$ (Figure 1B). This result demonstrates that the triplet pattern observed in the ESR spectra of **1a**$^+$ is caused by the protons of the central CH_2 group. In complete agreement with this assertion, we find that the ESR spectrum of **3**$^+$,[7] a molecule that *lacks* the central CH_2 group, displays only a singlet.

These results suggest symmetrical distribution of unpaired spin density in **1a**$^+$, at least on the hyperfine time scale ($>10^8$ s^{-1}), of which, judging from the sizeable magnitude of the hfs value, a substantial portion is located on the CH_2 group, by way of the half-filled orbital, similar to **4**, resulting from laticyclic hyperconjugative interactions. The strength of these interactions in **1a**$^+$, implied by the pes and ESR results, could well be such as to render **1a**$^+$ a fully charge delocalized symmetrical (C_{2v}) species.[10,11] This possibility receives additional support from model, albeit crude, ab initio MO calculations. Using the C_{2v} ethene···CH_4···ethene cation radical "complex" to mimic the hole-delocalized symmetrical (C_{2v}) **1a**$^+$, the UHF/6-31G** hfs[12a,b] for the bridge CH_2 hydrogens is 35 G, in excellent but perhaps fortuitous agreement with experiment[13] (the hfs for the vinylic hydrogens is calculated to be only −10 G). The "complex" minus one ethene molecule models the hole-localized, unsymmetrical (C_s) form of **1a**$^+$. The UHF/6-31G** hfs for the CH_2 group are now 12 G (for H that is closer to the double bond) and 8 G (for the more distant H) and that for the vinylic H's is −22 G. Rapid hole transfer (on the hyperfine time scale) between the two double bonds should give an average hfs of only 10 G for the CH_2 H's, a value much lower than the observed value of 30 G.[12c]

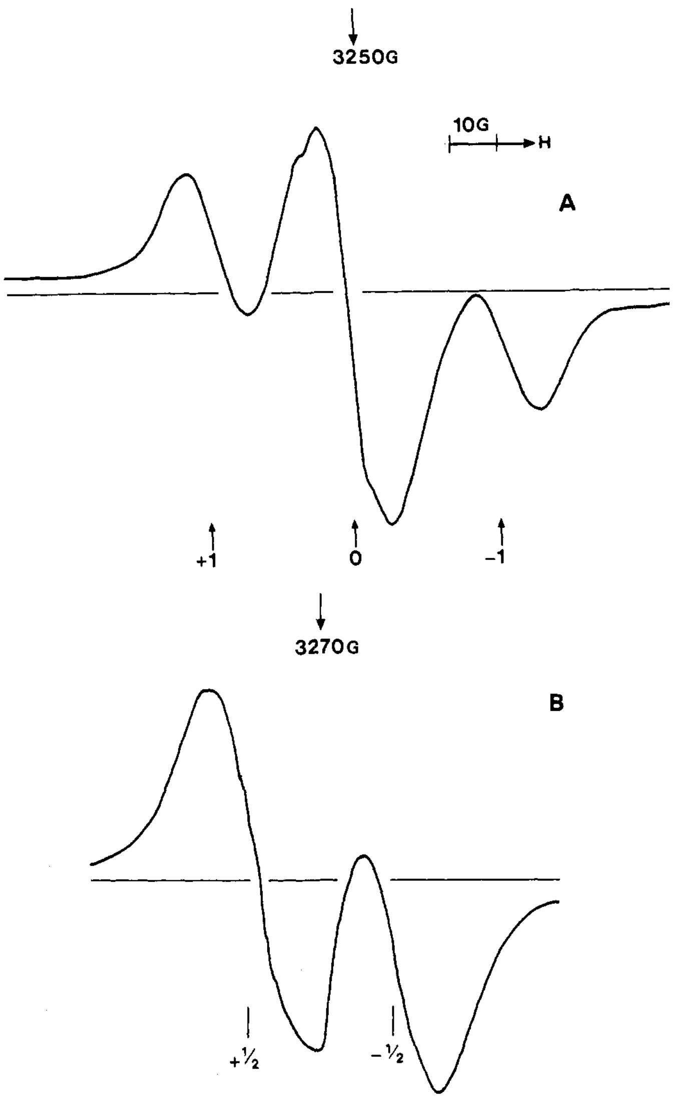

Figure 1. First derivative X-band ESR spectrum of dilute (1:1000) solutions of (a) **1a** and (b) **1b** in $CF_2ClCFCl_2$ after exposure to ^{60}Co γ rays at 77 K, showing (A) the $M_I(^1H) = +1, 0$, and -1 features assigned to **1a**$^+$ and (B) the $M_I(^1H) = +^1/_2$ and $-^1/_2$ features assigned to **1b**$^+$.

The data for **1a**$^+$, together with the sizeable π,π splitting observed for **2** (0.29 eV[1b,c]), suggest that hole transfer between the double bonds in **2**$^+$ might also be extremely rapid ($>10^8$ s^{-1}), notwithstanding their 9 Å separation, and this is being currently investigated. The finding of complete, or nearly complete, hole delocalization in **1a**$^+$, in which the double bonds are spatially remote from each other (ca. 6 Å) and are connected only via a supposedly "insulating" σ framework,[14] is quite remarkable since

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[7] Generated under conditions identical with those employed for generating **1a**$^+$.

[8] **1b** was synthesized via double Diels–Alder of hexachlorocyclopentadiene to 7-deuteronorbornadiene[9] and subsequent reductive dechlorination of the resulting bis adduct.[1d]

[9] Clarke, S. C.; Johnson, B. L. *Tetrahedron* **1968**, *24*, 5067.

[10] We cannot comment on the unpaired spin distribution in **3**$^+$, although the pes π,π splitting energy (ca. 0.2 eV[1a]) for **3** suggests that through-bond mediated hole transfer might also be very rapid in **3**$^+$.

[11] We hope soon to measure the ESR spectra of **1a**$^+$, **1b**$^+$, and **3**$^+$ at 4 K; such measurements should provide more definite information about the degree of hole delocalization in these species.

[12] (a) Isotropic hfs calculated from the Fermi contact terms obtained from the GAUSSIAN 86 suite of programs: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, C. M.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. GAUSSIAN 86, Carnegie-Mellon University: Pittsburgh, PA 15213. (b) These calculations were performed on the cation radical "complexes" by using geometries corresponding to optimized neutral ethene and methane. More extensive calculations are being carried out in collaboration with K. D. Jordan. (c) If anything, UHF hfs values tend to be overestimated, so that the experimental value could be less than 10 G.

[13] It should be pointed out that the experimental hfs values contain a contribution from dipolar coupling as well as from scalar coupling (as is clearly seen from the unsymmetrical nature of the triplet signal in the ESR spectrum of **1a**$^+$), whereas the SCF calculated values contain only scalar coupling contributions. Consequently, quantitative comparison between the experimental and the calculated hfs values should not be made. We thank a referee for mentioning this point.

[14] McConnell was the first to suggest that electron transfer between two unsaturated groups of anion radicals could be mediated by a connecting chain of CH_2 groups via a through-bond coupling mechanism: McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

it seems that only one other report of rapid intramolecular long-range positive hole transfer in cation radicals has been published.[15] This situation may be contrasted to the relatively large number of published reports of very rapid long-range intramolecular electron-transfer processes in anion radicals.[16a–c,17] This work provides yet another convincing demonstration that saturated groups are not "insulators" but can, in fact, be very efficient mediators in electron-transfer processes.[16] In this context, we believe that electron-transfer processes in general, not just positive hole transfer, can be strongly accelerated by laticyclic hyperconjugative interactions. The work described herein also indicates that perhaps there is something, after all, in the suggestion[3d,16e] that the very rapid electron-transfer steps in the photosynthetic reaction center could be mediated by the isoprenoid phytyl side chains of the special chlorophyll pair, bacteriopheophytin, and menaquinone, via a process similar to laticyclic hyperconjugation! The observation of long-range photoinduced electron transfer in molecular monolayers might also be a consequence of a type of laticyclic hyperconjugative interaction between adjacent alkyl chains.[18]

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(15) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173.

(16) (a) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670. (c) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (d) Hush, N. S.; Paddon-Row, M. N.; Cotsaris, E.; Oevering, H.; Verhoeven, J. W.; Heppener, M. *Chem. Phys. Lett.* **1985**, *117*, 8. (e) Warman, J. M.; de Haas, M. P.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. S.; Oevering, H.; Verhoeven, J. W. *Nature* **1986**, *320*, 615. (f) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (g) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061. (h) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366.

(17) (a) Shimada, K.; Szwarc, M. *Chem. Phys. Lett.* **1974**, *28*, 540. (b) Gerson, F.; Huber, W.; Martin, Jr., W. B.; Caluwe, P.; Pepper, T.; Szwarc, M. *Helv. Chim. Acta* **1984**, *67*, 416.

(18) (a) Mobius, D. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 848. (b) Kuhn, H. *J. Photochem.* **1979**, *10*, 111. (c) Kuhn, H. *Pure Appl. Chem.* **1979**, *51*, 341.

Relativistic Effects in Gold Chemistry. 2. The Stability of Complex Halides of Gold(III)

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The stability of the +III oxidation state in gold is unique within the group 11 elements. The halogen chemistry of copper and silver is restricted mostly to the oxidation state +I and +II. In contrast, the Au(I) compounds AuF and AuF_2^- have not been isolated although both AuF_3 and AuF_4^- exist.[1] There have been many attempts to rationalize these observations.[1–3] It has been shown in the first paper of this series[3] that relativistic effects are significant in determining the chemical and physical properties of gold. This communication demonstrates that the stability of the gold halide complexes in the +III oxidation state is mainly due to relativistic effects, as suggested as early as in 1978 by Pekka Pyykkö.[4]

Table I. Molecular Properties for the Square-Planar Gold(III) Halide Complexes AuX_4^- (X = F, Cl, Br, I)[a]

molecule	method	r_e	D_e	ΔU_0	D_e^{SO}	ΔU_0^{SO}	$\Delta_R \Delta U_0^{SO}$
F	NR	1.980	329.4	−81.3			
	R	1.930	523.5	116.6	519.1	113.7	195.0
Cl	NR	2.424	327.9	−100.1			
	R	2.344	496.4	80.3	485.9	73.3	173.4
Br	NR	2.549	292.4	−110.6			
	R	2.492	396.0	−13.3	352.9	−42.1	68.5
I	NR	2.830	220.3	−151.5			
	R	2.716	308.2	−38.9	217.2	−99.6	51.9

[a] Au–X bond distance r_e in Å, dissociation energy $D_e(AuX_4^- \rightarrow Au + 3X + X^-)$ in kJ mol^{-1}. ΔU_0 is given in eq 1. D_e^{SO} and ΔU_0^{SO} are the spin-orbit corrected D_e and ΔU_0 values using the Dirac–Fock atomic values calculated with program MCDF and the experimental spin-orbit splittings given in Moore's tables.[12]

Table II. Molecular Properties for the Linear Gold(I) Halide Complexes AuX_2^- (X = F, Cl, Br, I)[a]

molecule	method	r_e	D_e	D_e^1	D_e^2	D_e^{SO}	D_e^{2SO}
F	NR	2.236	410.7	247.6	163.1		
	NR/CISD[b]	2.215	460.4	207.7	252.7		
	NR/CISDSC	2.210	569.0	274.3	294.7		
	R	2.017	406.9	318.3	88.6	405.4	87.4
	R/CISD	2.028	483.2	316.5	166.7	481.6	165.1
	R/CISDSC	2.032	600.8	385.3	215.5	599.2	213.9
Cl	NR	2.630	428.0	210.1	217.9		
	R	2.398	416.1	255.4	160.7	412.6	157.2
Br	NR	2.750	403.0	200.3	202.7		
	R	2.526	382.2	228.1	157.2	367.8	142.8
I	NR	2.934	371.8	180.4	191.4		
	R	2.710	347.1	194.7	152.4	316.8	122.1

[a] Au–X bond distance r_e in Å, dissociation energy $D_e(AuX_2^- \rightarrow Au + X + X^-)$ in kJ mol^{-1}. D_e^1: dissociation energy for $AuX_2^- \rightarrow AuX + X^-$. D_e^2: $AuX \rightarrow Au + X$. $D_e = D_e^1 + D_e^2$. D_e^{SO} is the spin-orbit corrected D_e using the Dirac–Fock atomic values calculated with program MCDF and the experimental spin-orbit splittings given in Moore's tables.[12] [b] $r_e(AuF) = 2.160$ Å at the CISD level.[3]

Gold(III) compounds have a tendency to add a fourth ligand L to form stable four-coordinate AuX_3L complexes or to oligomerize to form gold(III) halogen-bridged compounds. The monomers AuX_3 (X = F, Cl, Br, I) have never been detected in the gas phase, indicating that the coordination number three is less favorable. This is supported by relativistic Hartree–Fock (HF) calculations showing that dimerization of the monomer AuF_3 would be favored by more than 160 kJ mol^{-1}.[5] Hence, the Au(III) halide complexes AuX_4^- (X = F, Cl, Br, I) have been chosen to discuss the stability of gold(III) species.

Nonrelativistic (NR) and relativistic (R) HF calculations using accurate pseudopotentials with a small core definition for gold, i.e., a [Xe4f^{14}] core,[3] have been performed for the Au(III) and Au(I) halide complexes in order to examine their relative stability according to eq 1. A modified version of GAUSSIAN86[6] has been

$$AuX_4^- \rightarrow AuX_2^- + 2X + \Delta U_0 \qquad (1)$$

used. The geometries are optimized by a Fletcher–Powell procedure.[6] The basis sets and pseudopotentials are given in the first paper of this series.[3] The calculated molecular properties for both series of complexes AuX_4^- and AuX_2^- (X = F, Cl, Br, I) are listed in Tables I and II, respectively.[7]

[†] Alexander von Humboldt Feodor Lynen fellow 1987–1989.

(1) (a) Puddephat, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978. (b) Puddephat, R. J. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, 1987; Vol. 5. (c) Uson, R.; Laguna, A. *Coord. Chem. Rev.* **1986**, *70*, 1. (d) Melnik, M.; Parish, R. V. *Coord. Chem. Rev.* **1986**, *70*, 157.

(2) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

(3) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.*, in press.

(4) Pyykkö, P. *Adv. Quantum Chem.* **1978**, *11*, 353.

(5) Schwerdtfeger, P., unpublished results.

(6) (a) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. program GAUSSIAN86, Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh PA, 1984, extended for local and nonlocal pseudopotentials by P. Schwerdtfeger by using program PSEPOT for the latter: Kolar, M. *Comput. Phys. Commun.* **1981**, *23*, 275. (b) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quant. Chem. Symp.* **1977**, *11*, 149.

0002-7863/89/1511-7261$01.50/0