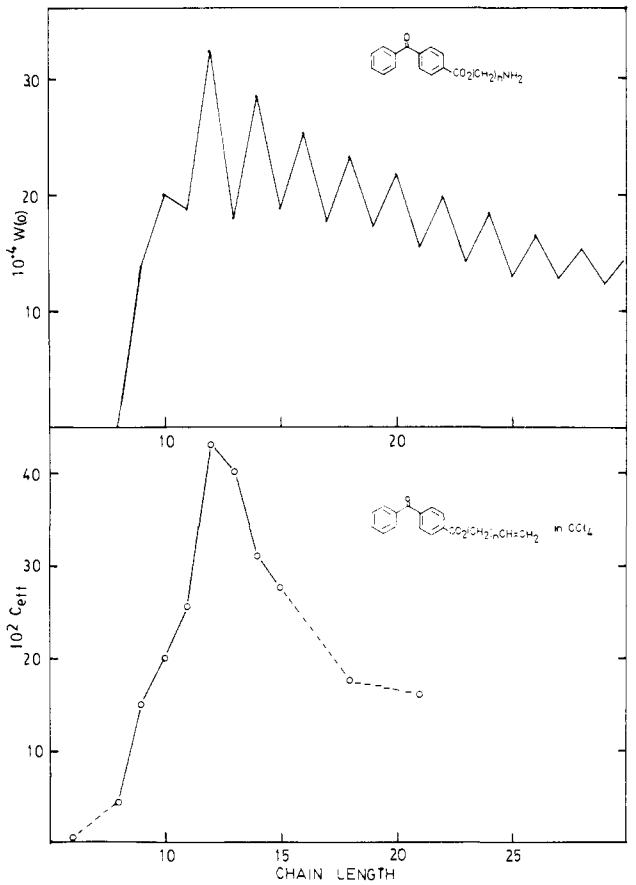

Figure 1. The upper part is a plot of the simulated cyclization probability $W(O)$ vs. chain length n for the molecules shown. Cyclization is detected by the presence of the nitrogen of the NH_2 group within 3.1 Å of the ketone carbonyl oxygen with its nonbonded electron pair directed toward that oxygen. Monte Carlo methods are used to estimate partition functions; see text. The lower part is a plot of $C_{eff} = k_0(n)/k_q^{(2)}$ for the quenching of aromatic ketone phosphorescence in CCl_4 solution at 25 °C.

to deviate from the gauche and trans rotational angles—and from the odd–even parity of diamonds lattice sites within the reactive volume. The model overestimates these oscillations. Real chains are able to undergo small torsional twists about each of its C–C bonds (Scheme I). The corresponding ΔS_{cy} values vary from −16 cal mol^{-1} K^{-1} for $n = 12$ to −18 cal mol^{-1} K^{-1} for $n = 30$.

Experimental results were obtained from flash photolysis experiments on **O-n** ($Q = -CH{=}CH_2$) at 10^{-3}–10^{-4} M in CCl_4 solution.[14,15] Exponential lifetimes τ_n were measured, and $1/\tau$ values were extrapolated to infinite dilution ($1/\tau_n^0$). Under these conditions

$$1/\tau_n^0 = 1/\tau_{Me} + k_{iq}(n)$$

where $\tau_{Me} = (k_p + k_d)^{-1}$ is the lifetime of the corresponding methyl ester **O**-(Me), and k_p and k_d are, respectively, the rate constants for radiative and radiationless decay of the chromophore. The term $k_{iq}(n)$ represents the chain length dependent rate constant for intramolecular phosphorescence quenching. A small fraction of $k_{iq}(n)$ is due to intramolecular hydrogen abstraction. Its contribution is known from our previous studies of molecules with $Q = CH_3$. We refer to the corrected values as $k_0(n)$. These describe quenching by Q and are proportional to the chain end-to-end cyclization probability. These values are plotted in the bottom half of Figure 1. What is particularly important about our results is that studies at various temperatures(from −20 to 100 °C) show that the *activation energy for intramolecular quenching is independent of chain length* (E_a = 2.6 kcal/mol) for $n > 8$. Hence the plot in the lower half of Figure 1 reflects only changes in cyclization entropy.

A more meaningful way of treating the experimental data is to normalize $k_0(n)$ values to remove the contribution of ketone excited-state reactivity.[3a] This can be done by dividing $k_0(n)$ by the second-order rate constant $k_q^{(2)}$ for the reaction of **O**-Me with an appropriate model alkene. For this purpose we have chosen 1-pentene. The $k_q^{(2)}$ value of 1.6×10^7 M^{-1} s^{-1} for this reaction is 1000 times smaller than that for a diffusion controlled reaction and emphasizes that a conformational equilibrium is reached in the excited state of **O**-n before reaction. The ratio $[C_{eff} = k_0(n)/k^{(2)}]$ has units of mol/L. It represents the effective concentration of the quencher Q in the reactive volume about the C=O group. While this volume is not known, one can calculate that a C_{eff} value of 1×10^{-2} M corresponds to a P_n value of 1×10^{-4} in a reactive volume of 17 Å^3. This value for the size of the reactive volume is not unreasonable and emphasizes that in spite of the simplifying assumptions, the lattice-based rotational isomeric state model is able to simulate effectively both qualitative and quantitative features of end-to-end cyclization in molecules like **O**-n.

Acknowledgment. We thank NSERC Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

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^{197}Au Mössbauer Spectroscopic Data for Antiarthritic Drugs and Related Gold(I) Thiol Derivatives

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Gold(I) thiolates (AuSR) have been used for many years in the production of decorative finishes to ceramics, etc. More recently, compounds of this type in which SR is, for example, a thiomalate or a substituted thioglucose group have attracted considerable attention for the treatment of rheumatoid arthritis and inflammatory disorders.[1-6] Despite this importance, very little is known of the structures of any of these thiolates. X-ray crystallography has shown that an analogous silver compound, $AgSC_6H_{11}$, has a polymeric structure involving both two- and three-coordinate silver,[7] but the gold thiolates have not been crystallized. However, Mössbauer spectroscopy with ^{197}Au has been shown to be well suited to the determination of structures of gold compounds,[8] and we now present data for a variety of gold(I) thiolates, including some of the drugs in current use. The data establish polymeric structures with linear coordination at gold.

Previous studies have shown that, in combination, the isomer shift (IS) and quadrupole splitting (QS) are diagnostic of the number and type of ligands bound to gold (ref 8 and references

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Table I. ^{197}Au Mössbauer Parameters (4.2 K)

compd	IS,[a,b] mm s^{-1}	QS,[b] mm s^{-1}	Γ,[c] mm s^{-1}	ref
$AuSCH_2CH_3$	2.99	6.48	1.99, 2.16	
$AuSCH(CH_3)_2$	3.09	6.81	2.00, 2.17	
$AuS(CH_2)_3CH_3$	3.08	6.69	1.95, 2.21	
$AuSC_6H_5$	2.71	6.24	1.72, 2.01	
$AuSCH_2CO_2H$	2.98	6.71	2.02, 2.23	
$AuS(CH_2)_2NH_3^+Cl^-$	2.86	6.48	1.88, 2.04	
$AuSCH_2CH(NH_3^+)CO_2^-$	2.87	6.47	2.12, 2.36	
$AuSCH_2CH(NHCO{\cdot}CH_3)CO_2H$	2.97	6.51	1.90, 2.18	
Au(glut)[d]	2.86	6.43	1.91, 2.12	
$AuSCH(CO_2^-Na^+)CH_2CO_2^-Na^+{\cdot}H_2O{\cdot}{}^1/_3C_3H_8O_3$ (Myocrisin)				
	2.91	6.53	2.12, 2.56	
	2.8	6.5		*e*
$AuSCHOCH(CH_2OH)(CHOH)_2CHOH$ (Solganol)				
	2.57	6.19	2.08, 2.53	
	2.5	6.1		*e*
$Na_3[Au(S_2O_3)_2]$ (Sanochrysin)	3.13	7.01	1.97, 1.90	
	1.93	7.08		*f*
$Et_3PAuSCHOCH(CH_2OAc)(CHOAc)_2CHOAc$ (Auranofin)				
	4.80	8.77	1.95, 2.05	
	4.7	8.8		*e*
$[AuS_2CNEt_2]_2$	2.92	5.98		*g*
	2.89	6.02		*h*
$[AuS_2CNPr_2]_2$	3.00	6.39		*g*
$[AuS_2CNBu_2]_2$	2.84	5.94		*g*
$[AuS_2COC_8H_{17}]_2$	2.64	6.16		*g*
$Ph_4P[AuCS_3]$	3.13	6.43		*g*
$(Ph_4P)_2[Au_2(WS_4)_2]$	2.08	5.58		*g*
$(Ph_4As)_2[Au_2(WS_4)_2]$	2.32	5.71		*g*
$AuS_2P(OR)_2$	2.18	6.09		*g*
$[Au(SPPh_3)_2]PF_6$	2.46	6.82		*i*
$[Au(S{:}CNHCH_2CH_2NH)_2]PF_6$	2.77	7.49		*i*
$[Au(SMe_2)_2]PF_6$	3.43	7.56		*i*

[a] Relative to gold foil. [b] ±0.03 mm s^{-1}. [c] ±0.06 mm s^{-1}. [d] glut = glutathionate, $SCH_2CH(CO{\cdot}NHCH_2CO_2H)NH{\cdot}CO(CH_2)_2CH(NH_3^+)CO_2^-$. [e] Hill, D. T.; Sutton, B. M.; Sadler, P. J.; Calis, G. H. M.; Trooster, J. M. "Abstracts of Papers"; 179th National Meeting of the Americal Chemical Society, Houston, 1980; American Chemical Society: Washington, DC, 1980; Abstr, MEDI 16. [f] Faltens, M. O.; Shirley, D. A. *J. Chem. Phys.* 1970, *53*, 4249. The IS of this report seems to be in error. [g] Viegers, M. P. A. In "Mössbauer Spectroscopy and Transition Metal Chemistry"; Gütlich, P., Link, R., Trautwein, A., Eds.; Springer-Verlag: Berlin, 1978; p 209. [h] Parish, R. V.; Rush, J. D., unpublished data. [i] Jones, P. G.; Maddock, A. G.; Mays, M. J.; Muir, M. M.; Williams, A. F. *J. Chem. Soc., Dalton Trans.* 1977, 1434.

therein). For two-coordinate systems there is a good, almost linear, positive correlation between the two parameters; hard ligands (e.g., halides) give low values for both parameters, and soft ligands, (phosphines, cyanide ion) give high values. Three-coordinate complexes give a similar correlation but with a steeper slope: for complexes of the same ligand, three-coordination gives a similar QS to that for two-coordination but a markedly smaller IS.[8] The data for the thiol derivatives AuSR lie well within the band of values characteristic of two-coordination and are very similar to those for complexes which are known to involve gold coordinated by two S-donor ligands (Table I). Thus, the thiol derivatives must have polymeric structures, –S(R)–Au–S(R)–Au–, with linear, or almost linear, two-coordination at gold. The environment of the gold atom must be similar to that found by X-ray analysis for $Na_3[Au(S_2O_3)_2]$,[9] and $[Au(S_2CNR_2)]_2$,[10,11] and suggested by recent EXAFS data for Myocrisin.[12] Three-coordination would be expected to give an IS lower by about 1 mm s^{-1} and is clearly

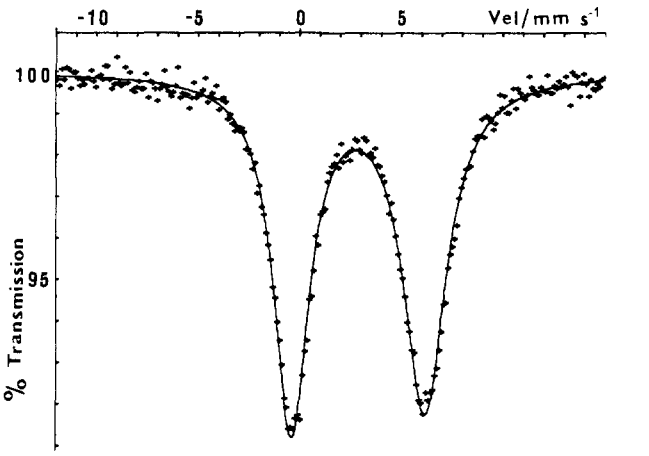

Figure 1. ^{197}Au Mössbauer spectrum of Myocrisin at 4.2 K. Note the broadening of the higher velocity peak. The solid line is a sum-of-two Lorentzian fit.

not present. The structures are thus different from that of $[AgSC_6H_{11}]_n$, which involves two- and three-coordinate silver in 1:2 ratio.[7]

All the compounds $[AuSR]_n$ give similar Mössbauer spectra, regardless of whether the group R is a simple organic group, an amino-acid group, or a carboxylate salt; thus, the pharmacological compounds are no different from the conventional thiolates, at least as far as the coordination of the gold atom is concerned. The spectra of Myocrisin and Solganol are quite asymmetric. The two absorptions are of equal area but that at higher velocity is significantly broadened (Figure 1). This presumably indicates more than one environment for the gold atoms and could result from different types of polymers being present in the solid or, more probably, from slight variations in bond angle and bond length within a single polymer unit. Inspection of the data for the other thiolates (Table I) shows a similar broadening of the higher velocity peak in all cases; again, the areas of the two peaks are equal. The broadening is independent of sample thickness and appears not to be an instrumental effect: spectra of nonpolymeric materials, including those of Auranofin and Sanochrysin, are more symmetrical. For Myocrisin and Solganol, fitting of the data is improved by the addition of a second component under the broader peak, i.e., fitting as two doublets whose low-velocity peaks superpose. Both sets of parameters are consistent with two-coordination, and further refinement of the data is in progress.

An intriguing aspect of the thiolates is their wide variation in solubility. When the group R is a small organic group, the compounds are extremely insoluble in all solvents, but solubility is improved by the introduction of appropriate substituents. Large organic groups (e.g., 4-*tert*-butylphenyl) confer solubility in organic solvents,[13] while carboxy or hydroxy substituents allow solubility in water. These trends are in keeping with the nature of the substituents and imply the presence of relatively small polymeric units. Such units would presumably be ring oligomers, and structures with about six AuSR groups seem likely. Cryoscopic measurements with gold thiomalate suggest an octameric unit.[14] The amino acid derivatives are soluble only at very high or very low pH.[2,15,16] Since at moderate pH values these compds. will exist in the highly polar zwitterionic form, $-C(NH_3^+)-CO_2^-$, insolubility under these conditions seems anomalous. The intramolecular interactions between adjacent negatively and positively charged groups may serve to open the Au–S–Au angle and lead to larger polymeric units and insolublity. At the extremes

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of the pH range, either the $-NH_3^+$ group is deprotonated or the $-CO_2^-$ group is protonated, the interactions are diminished, and rearrangement may be possible to a smaller, more soluble form. In materials such as Myocrisin, adjacent substituents bear negative charges ($-CO_2^-$), giving repulsive interactions; in these cases, smaller cyclic units are likely, consistent with their ready solubility.

The ^{197}Au Mössbauer spectrum of Auranofin is consistent with the linear S-Au-P stereochemistry recently established by X-ray crystallography.[17]

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Bis(2,2′-bipyridyl)diisopropoxymolybdenum(II). Structural and Spectroscopic Evidence for Molybdenum-to-Bipyridyl π^* Bonding

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During the course of work aimed at preparing compounds related to $Mo(OBu\text{-}t)_2(py)_2(CO)_2$,[1] we discovered that hydrocarbon solutions of $Mo_2(OPr\text{-}i)_6$[2] (M≡M) and bpy (2,2′-bipyridine) react[3] to give deep-purple solutions from which crystals of $Mo(OPr\text{-}i)_2(bpy)_2$ are obtained in near quantitative yield, based on reaction 1.

$$Mo_2(OPr\text{-}i)_6 + 2bpy \rightarrow Mo(OPr\text{-}i)_2(bpy)_2 + {}^1/_2Mo_2(OPr\text{-}i)_8 \quad (1)$$

The cleavage of the Mo≡Mo bond is noteworthy since monodentate ligands, such as pyridine, are known to form adducts of the type $Mo_2(OR)_6L_2$ with retention of the triple bond.[4]

$Mo(OPr\text{-}i)_2(bpy)_2$ is an air-sensitive, paramagnetic, dark-purple crystalline solid, sparingly soluble in alkane solvents, but very soluble in benzene and toluene. Its color is derived from an intense band at λ_{max} 530 nm (ϵ 10000).

The molecular structure in the solid state revealed[5] a distorted octahedral geometry for the central MoO_2N_4 skeleton. An ORTEP view of the molecule is shown in Figure 1, and pertinent distances and angles associated with the central MoO_2N_4 skeleton are given in Table I. The Mo–O distances are short, comparable to those in $Mo(OBu\text{-}t)_2(py)_2(CO)_2$, which implies significant oxygen-p-to-molybdenum-d π bonding. The alkoxy ligands, however, are cis in $Mo(OPr\text{-}i)_2(bpy)_2$ and trans in $Mo(OBu\text{-}t)_2(py)_2(CO)_2$. The Mo–N distances in $Mo(OPr\text{-}i)_2(bpy)_2$ are short, 2.12 Å (average), which may be compared to Mo–N = 2.35 Å (average) in $Mo(OBu\text{-}t)_2(py)_2(CO)_2$.

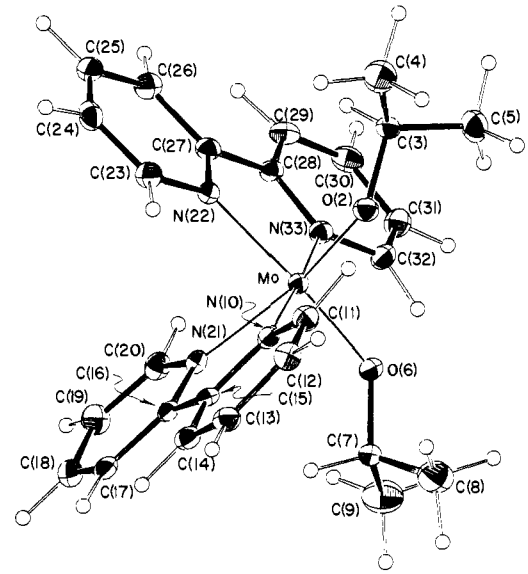

Figure 1. ORTEP view of the $Mo(OPr\text{-}i)_2(bpy)_2$ molecule showing the atom numbering scheme used in the tables.

Table I. Bond Distances (Å) and Angles (Deg) Associated with the Central MoO_2N_4 Skeleton of the $Mo(OPr\text{-}i)_2(bpy)_2$ Molecule

A	B	dist
Mo(1)	O(2)	1.942 (2)
Mo(1)	O(6)	1.932 (2)
Mo(1)	N(10)	2.107 (2)
Mo(1)	N(21)	2.123 (2)
Mo(1)	N(22)	2.126 (2)
Mo(1)	N(33)	2.115 (2)

A	B	C	angle
O(2)	Mo(1)	O(6)	105.3 (1)
O(2)	Mo(1)	N(10)	85.1 (1)
O(2)	Mo(1)	N(21)	155.4 (1)
O(2)	Mo(1)	N(22)	91.6 (1)
O(2)	Mo(1)	N(33)	97.9 (1)
O(6)	Mo(1)	N(10)	97.0 (1)
O(6)	Mo(1)	N(21)	90.2 (1)
O(6)	Mo(1)	N(22)	153.7 (1)
O(6)	Mo(1)	N(33)	84.3 (1)
N(10)	Mo(1)	N(21)	73.9 (1)
N(10)	Mo(1)	N(22)	104.5 (1)
N(10)	Mo(1)	N(33)	176.2 (1)
N(21)	Mo(1)	N(22)	81.6 (1)
N(21)	Mo(1)	N(33)	102.6 (1)
N(22)	Mo(1)	N(33)	73.3 (1)

A close inspection of the interatomic distances associated with the bpy ligands revealed small but systematic deviations from those distances found in either the free ligand[6] or any of its structurally characterized coordination compounds involving the transition elements.[7] This observation prompted us to redetermine the structure of 2,2′-bipyridine[8] in order to make a more accurate

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