1606 Inorganic Chemistry, Vol. 10, No. 8, 1971

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A Raman Study of Metal–Metal Bonding in Gold(I) Diisobutyldithiocarbamate Dimer[1]

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Received February 19, 1971

Gold(I) diisobutyldithiocarbamate is known to have a dimeric structure, in which the gold atoms are only 2.76 Å apart. Its Raman spectrum in chloroform solutions shows four of the five totally symmetric (A_1) modes expected for the central $Au_2(S_2C-)_2$ unit, including a moderately intense band assignable to Au–Au stretching. On the basis of an approximate normal-coordinate analysis, the A_1 Raman intensities have been used to calculate bond polarizability derivatives. The Au–Au bond order is estimated at about one-fourth of its value in Au_2^0. The metal–metal interaction can be understood on the basis of charge transfer from the dithiocarbamate ligands to the gold(I) ions, with the partial formation of an Au_2^0 bond.

Introduction

Recent studies from this laboratory[2–7] have been concerned with evaluating the extent of metal–metal interaction in polynuclear complexes from their Raman spectra. From absolute Raman intensities of totally symmetric vibrational modes one can evaluate molecular and bond polarizability derivatives and estimate bond orders. These procedures led to the inference of metal–metal interaction in the cage complexes $[(CH_3)_3PtOH]_4$,[2] $[(CH_3)_3PtCl]_4$,[2] $Tl_4(OC_2H_5)_4$,[3] and $Pb_4(OH)_4^{4-}$ [3] (all T_d) and $Bi_6(OH)_{12}^{6+}$ (O_h).[3] The interaction is much less than in the unequivocally metal–metal bonded molecules $M_2(CH_3)_6$ (M = Si, Ge, Sn),[4] $M_2(C_6H_5)_6$ (M = Sn, Pb),[5] $M_2(CO)_{10}$ (M = Mn, Re),[3] and the (aq)Hg_2^{2+} ion.[3] This is as expected considering the large internuclear separations in the cage complexes and the stability of the metal valence states, $5d^6$ for Pt(IV) and $5d^{10}6s^2$ for Tl(I), Pb(II), and Bi(III). That the metal–metal interaction is nevertheless significant is suggested by studies of analogous complexes of noble gas ions, in which metal–metal interaction is precluded: $M_6O_{19}^{8-}$ (M = Nb, Ta)[6] and $M_4(OH)_8(H_2O)_{16}^{8+}$ (M = Zr, Hf).[7] For these species the modes which are primarily associated with changes in the metal–metal distances are very weak or absent in the Raman spectra.

An interesting complex from the point of view of metal–metal bonding is the binuclear *N*,*N*-diisobutyldithiocarbamate ($S_2CN(C_4H_9)_2$) of gold(I). Its structure is reported to be the same as that of its *n*-propyl analog,[8,9] which is shown in Figure 1. The valence state of Au(I), $5d^{10}$, is quite stable and would not normally be expected to favor homonuclear metal–metal bonds. (Many heteronuclear gold(I)–metal bonds are known, but substantial electronegativity differences are involved.) Nevertheless the Au–Au distance in $Au_2(S_2CN(C_4H_9)_2)$, 2.76 Å, is less than that found in metallic gold,[10] 2.88 Å. Furthermore the Au–Au separation is substantially less than the S–S span, 3.05 Å, of the $S_2CN(C_4H_9)_2$ ligands, although the S–Au–S bonds are collinear, as expected for Au(I). The shortening of the Au–Au distance is accomplished by twisting the ligands relative to each other by 16.5°, so that the sulfur atoms are out of the plane containing the carbon and gold atoms. There seems little to account for this out-of-plane twist except mutual interaction of the gold atoms.

We present here a Raman study of $Au_2(S_2CN(C_4H_9)_2)$ aimed at evaluating the degree of Au–Au interaction.

Experimental Section

Gold(I) dithiocarbamate was synthesized according to Åkerstrom[8] and recrystallized from benzene and petroleum ether (mp 170°, lit.[8] mp 172°). Infrared spectra were obtained in KBr pellets and Nujol mulls with a Beckman IR-12 spectrophotometer. Raman spectra were obtained for the crystalline solid and for 0.4 *M* solution in chloroform. The Raman spectrometer and its calibration have been described elsewhere.[3] He-Ne (6328 Å) (Spectra Physics Model 125) and Ar^+-Kr^+ (6764, 6471, 5682, 5308, 4880 Å) (Coherent Radiation Model 52) laser excitation was used. Depolarization ratios were obtained by analyzing the scattered light with a Polaroid disk. Intensities of the Raman bands were measured from the recorded spectra using a polar planimeter. The ν_6 (262 cm^{-1}) line of the chloroform solvent was used as an internal standard.

Spectra and Assignments

The vibrational modes associated primarily with the central $Au_2(S_2C-)_2$ unit of $Au_2(S_2CN(C_4H_9)_2)_2$, with which this study is concerned, are expected to lie below 1000 cm^{-1}. Raman and infrared frequencies found in this region are listed in Table I. The Raman spectrum of a chloroform solution is shown in Figure 2. The spectrum of the solid was similar but there was high background scattering.

TABLE I

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS BELOW 1000 CM^{-1} FOR $Au_2(S_2CN(C_4H_9)_2)_2$

Raman[a]		Infrared[b]	
		875 m	
		850 w	
813 p, m[c]	ν_{C-S}	825 w	
762 s	ν_{C-S}	625 m	
		605 sh	
440 p, s	δ_{S-C-S}	440 m	δ_{S-C-S}
340 p, s	ν_{Au-S}	375 w	ν_{Au-S}
328 m	ν_{Au-S}	337 s	ν_{Au-S}
185 p, m	ν_{Au-Au}	320 m	δ_{N-C-S}
138 s	δ_{Au-S-C}		

[a] Chloroform solution. [b] Nujol mull. [c] Symbols: p, polarized (A_1); s, strong; m, medium; w, weak; sh, shoulder.

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[1] This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Sciences, and by National Science Foundation Grant GP-10122.

[2] P. A. Bulliner, V. A. Maroni, and T. G. Spiro, *Inorg. Chem.*, **9**, 1887 (1970).

[3] C. O. Quicksall and T. G. Spiro, *ibid.*, **9**, 1045 (1970).

[4] B. Fontal and T. G. Spiro, *ibid.*, **10**, 9 (1971).

[5] P. A. Bulliner and T. G. Spiro, *ibid.*, **10**, 13 (1971).

[6] F. J. Farrell, V. A. Maroni, and T. G. Spiro, *ibid.*, **8**, 2638 (1969).

[7] F. J. Farrell and T. G. Spiro, submitted for publication.

[8] S. Åkerstrom, *Ark. Kemi*, **14**, 387 (1959).

[9] R. Hesse in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 314.

[10] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11**, S3 (1958).

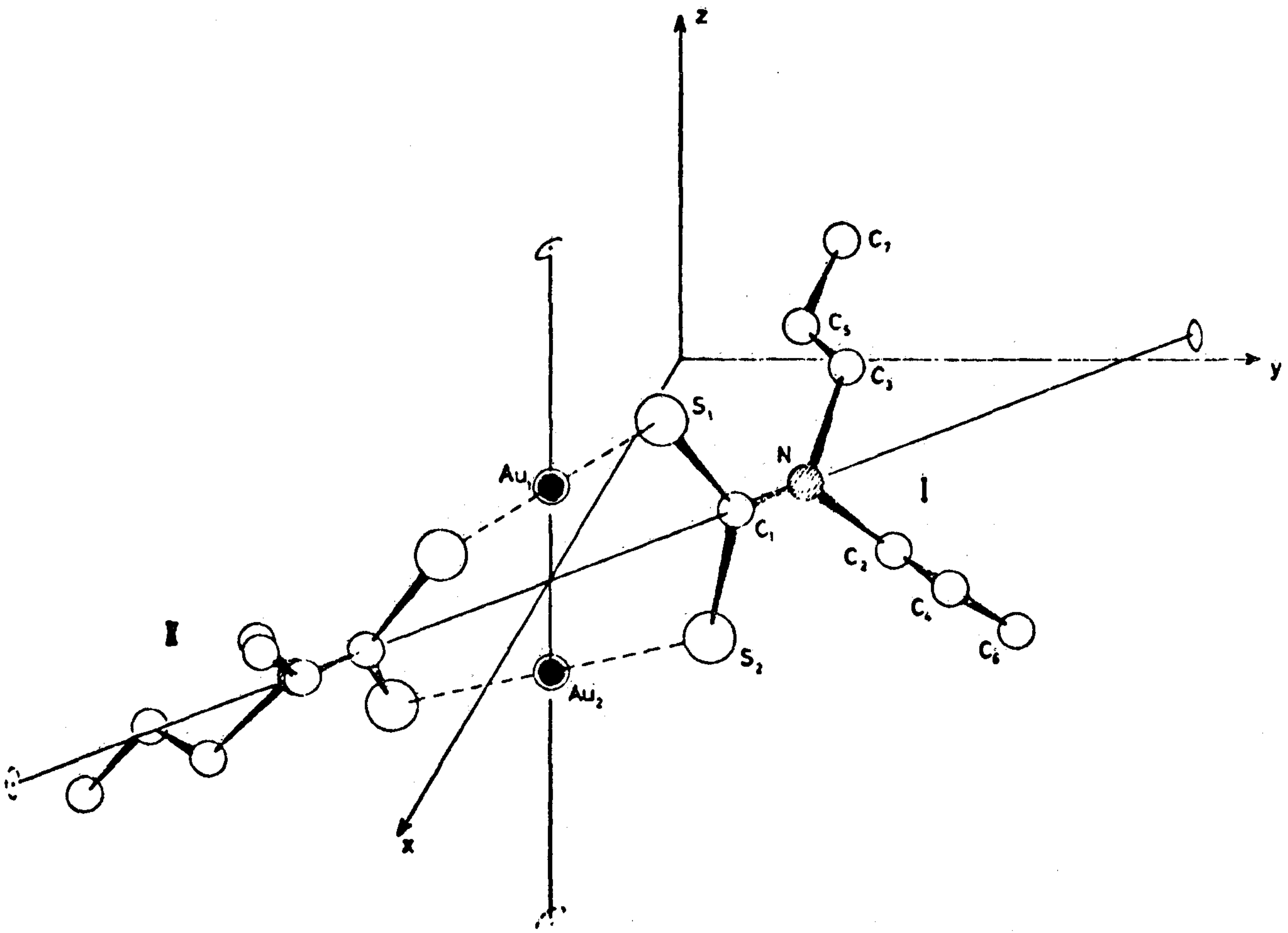

Figure 1.—Structure of gold(I) *N,N-n*-propyldithiocarbamate, taken from ref 9.

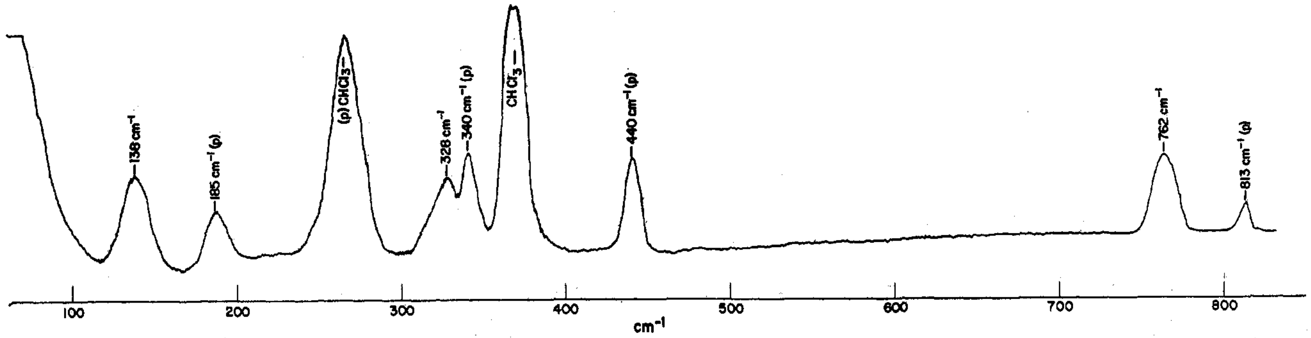

Figure 2.—Raman spectrum of 0.4 *M* $Au_2(S_2CN(C_4H_9)_2)_2$ in $CHCl_3$, with 5682-Å Ar^+–Kr^+ laser (Coherent Radiation Model 52) excitation, a slit width of 12 cm^{-1}, a scanning rate 10 cm^{-1}/min, and a time constant of 2 sec.

The approximate point symmetry of $Au_2(S_2CN(C_4H_9)_2)_2$ is D_2 (neglecting hydrogen atoms and carbon atoms beyond those attached to the nitrogen atoms). The contributions of internal coordinates of the $Au_2(S_2C-)$ unit to the symmetry species of D_2 are given in Table II. As always in cyclic molecules there are redundancies among the sides and angles of the rings. In the internal coordinate set of Table II, as in the normal-coordinate analysis below, we have chosen to neglect S–Au–Au and S–Au–S bending. Their contributions can be expressed in terms of the other coordinates, through the redundancy conditions.

TABLE II

CONTRIBUTIONS OF INTERNAL COORDINATES IN $Au_2(S_2C-)_2$ TO D_2 SYMMETRY SPECIES

	A_1	B_1	B_2	B_3
C–S str	1	1	1	1
Au–S str	1	1	1	1
Au–Au str	1	0	0	0
S–C–S bend	1	0	0	1
Au–S–C bend	1	1	1	1
Total	5	3	3	4

Assignments are facilitated by reference to the normal-coordinate analysis of $Pt(S_2CNH_2)$ by Nakamoto, *et al.*[11] The four polarized (A_1) Raman bands at 813, 440, 340, and 185 cm^{-1} can be identified approximately at ν_{C-S}, δ_{S-C-S}, ν_{Au-S}, and ν_{Au-Au}, respectively. The fifth predicted A_1 mode (δ_{Au-S-C}) is not observed and is presumably below 80 cm^{-1}, where the wing of the Raman exciting line interferes. The

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[11] K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).

nontotally symmetric Raman bands at 762 and 329 cm^{-1} can be associated with C–S and Au–S stretching, while the one at 138 cm^{-1} probably involves a combination of Au–S–C and S–Au–S bending. In the infrared spectrum the band at 320 cm^{-1} may be largely N–C–S bending (δ_{N-C-S} 306 cm^{-1} in $Pt(S_2CNH_2)_2$).[11] The ir bands at 337 and 375 cm^{-1} complement the Raman bands at 328 and 340 cm^{-1} to make up the four expected Au–S stretching modes. The apparent mutual exclusions may be understood if the modes are considered as the coupled symmetric and asymmetric stretches of two linear S–Au–S units. The 440-cm^{-1} ir band is coincident with the A_1 δ_{S-C-S} band. Two S–C–S bending modes are expected but they may be accidentally degenerate since coupling across the gold atoms should be slight. The five ir bands from 605 to 875 cm^{-1} are difficult to assign. Four C–S stretching modes are expected in this region, but they probably occur in degenerate pairs (again because of weak coupling across the gold atoms) and should be coincident with the corresponding Raman frequencies. In fact no coincidences are observed. A large number of modes are expected for the isobutyl groups attached to the nitrogen atoms, and some of these modes should occur in the 600–900-cm^{-1} region, particularly those involving CH_3 and CH_2 torsions.[12]

It should be noted that ν_{C-S} (A_1) is nearly 200 cm^{-1} higher for $Au_2(S_2CN(C_4H_9)_2)_2$ than for $Pt(S_2CNH_2)$,[11] while δ_{S-C-S} (A_1) is 100 cm^{-1} lower. The differences can be explained on the basis of geometry-dependent kinetic interaction among C–S and M–S stretching and S–C–S bending coordinates. The Au–S–C angle is much larger than the Pt–S–C angle and permits greater coupling of the modes. As shown in the following section, the force constants are nevertheless very similar for the two complexes. The low Raman intensity of ν_{C-S} (A_1) (see Figure 2) is also due to coupling and to opposing bond polarizability contributions. The intensity analysis below shows that the C–S bond polarizability derivative is, if anything, too high.

Normal-Coordinate Analysis

An approximate normal-coordinate analysis was performed on the A_1 frequencies, in order to obtain reasonable eigenvectors with which to sort out the contributions of the internal coordinates to the molecular polarizability derivatives. All atoms except for those in the $Au_2(S_2C-)_2$ unit were neglected in the calculation. The work of Nakamoto, *et al.*,[11] shows that N–C stretching mixes very little into the $M(S_2C-)$ modes. (Mixing of N–C–S bending is more significant, but this coordinate does not contribute to A_1 modes.) The coordinates involving the isobutyl groups should mix even less.

Table III

Molecular Parameters[8,9] for $Au_2(S_2C-)_2$

Atoms	Distance, Å	Atoms	Angle, deg
C–S	1.70	S–C–S	122
Au–S	2.46	Au–S–C	117
Au–Au	2.76	S–Au–S	180

Molecular parameters are given in Table III. Schachtschneider's programs[13] GMAT and FPERT were used for construction of the G matrix and for solution of the A_1 block of the secular equation. The symmetry force constants for C–S, Au–S, and Au–Au stretching and for S–C–S bending were adjusted to calculate the four observed A_1 frequencies. Since the fifth A_1 frequency (Au–S–C bending) was unobserved, the corresponding force constant could not be reliably fixed. However it proved impossible to calculate the higher two frequencies (813 and 440 cm^{-1}) with reasonable values for F_{C-S} and F_{S-C-S} if F_{Au-S-C} was set at zero. Coupling of the C–S and S–C–S coordinates with Au–S–C bending is significant and introduction of a reasonable value for F_{Au-S-C} eliminated the discrepancy. The calculated value of the fifth A_1 frequency was below our spectral limit, as expected. Table IV compares observed and calculated frequencies and lists the adjusted values of the force constants. The agreement of our force constants with those reported for $Pt(S_2CNH_2)_2$ by Nakamoto, *et al.* (3.00, 2.10, 0.52, and 0.15 mdyn/Å for K_{C-S}, K_{Pt-S}, H_{S-C-S}, and H_{Pt-S-C}, respectively),[11] is better than could have been expected, considering that the latter are from a Urey–Bradley force field. The eigenvectors are given in Table V. They show that the Au–Au and Au–S modes are faily pure but that the C–S, S–C–S, and Au–S–C modes are highly mixed.

Table IV

Normal-Coordinate Analysis Results for the A_1 Frequencies of $Au_2(S_2C-)_2$

	A_1 freq, cm^{-1}		Symmetry force const, mdyn/Å	
	Obsd	Calcd		
Q_1	813	820	F_{C-S}	3.00
Q_2	440	440	F_{Au-S}	2.26
Q_3	340	341	F_{Au-Au}	1.95
Q_4	185	188	F_{S-C-S}	0.52
Q_5	. . .	30	F_{Au-S-C}	0.44

Table V

Eigenvector Elements for the A_1 Modes of $Au_2(S_2C-)_2$

	Q_1[a]	Q_2	Q_3	Q_4	Q_5
S_{CS}[b]	0.211	−0.149	−0.018	0.006	0.002
S_{SCS}	−0.336	−0.079	0.021	0.020	0.012
S_{AuS}	−0.067	0.011	−0.167	0	0
S_{AuAu}	0.004	0.010	−0.001	0.101	−0.004
S_{AuSC}	0.232	0.131	−0.006	0.014	0.012

[a] Normal modes numbered in order of decreasing frequency (see Table IV). [b] A_1 symmetry coordinates generated from the internal coordinates indicated by the subscripts.

Polarizability Derivatives

Molecular polarizability derivatives, $\bar{\alpha}'_Q$, were calculated (Table VI) from the intensities and depolariza-

Table VI

Intensities and Molecular Polarizability Derivatives

Normal mode	R[a]	$\bar{\alpha}'_Q$, Å^2 amu$^{-1/2}$	ρ_l[b]
Q_1	0.855	0.484	0.196
Q_2	7.61	1.140	0.089
Q_3	9.87	1.026	0.019
Q_4	4.51	0.439	0.129

[a] R is the molar intensity relative to ν_6 of $CHCl_3$

$$R_i = \frac{I_i}{M_i}\frac{M_{CHCl_3}}{I_{\nu_6}(CHCl_3)}$$

where I is measured intensity and M is molarity. [b] ρ_l is the depolarization ratio for polarized incident light and analyzed scattered light.

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(12) V. Anthoni, *Acta Chem. Scand.*, **20**, 2742 (1966).

(13) J. H. Schachtschneider, Technical Reports No. 231-64 and 57-65, Shell Development Co., Emeryville, Calif., 1964–1965.

tion ratios of the A_1 bands in the usual manner[14] and placed on an absolute scale by comparison with ν_6 (262 cm^{-1}) of chloroform ($\bar{\alpha}'_Q = 0.364$ determined by comparison with ν_1 of CCl_4 ($\bar{\alpha}'_Q = 0.686$)[15] in a mixture of $CHCl_3$ and CCl_4). Solutions of $Au_2(S_2CN(C_4H_9)_2)$ are yellow and resonant enhancement of the Raman intensities was suspected in the light of recent examples of this effect in metal–metal bonded molecules with electronic transitions in the near-ultraviolet spectrum.[3,6] However no significant variation in the $\bar{\alpha}'_Q$ values was observed for excitation at different frequencies between 6764 and 4880 Å. Therefore, a resonance effect is excluded. The molecular polarizability derivatives were converted to internal coordinate polarizability derivatives, $\bar{\alpha}'_u$, *via* the transformation[14]

$$\bar{\alpha}'_{Q_i} = \sum_j \sqrt{N_j}\,\bar{\alpha}'_{u_j} l_{ji} \qquad (1)$$

where N_j is the number of internal coordinates, u_j, in the symmetry coordinate S_j, and l_{ji} is the eigenvector element describing the displacement of u_j in the normal mode Q_i.

There are as many simultaneous eq 1 as there are A_1 normal modes. Furthermore the sign of $\bar{\alpha}'_Q$ is undetermined because Raman intensity is proportional to the square of $\bar{\alpha}'_Q$. For n simultaneous equations there are therefore 2^n solutions, divided into 2^{n-1} pairs which differ only in sign. In the present case, there are five unknowns but only four equations, since the lowest frequency A_1 mode is unobserved. Therefore $\bar{\alpha}'_{Au-S-C}$ was arbitrarily set equal to zero, in accord with the assumption of the Wolkenstein bond polarizability theory[14] that angle bending does not contribute to $\bar{\alpha}'_Q$. Of the eight pairs of solutions all but two could be eliminated as physically unreasonable. The positive members of each of the acceptable pairs of solutions are given in Table VII.

TABLE VII

INTERNAL COORDINATE POLARIZABILITY DERIVATIVES AND BOND ORDERS

Internal coordinate	$\bar{\alpha}'_u$,[a] Å^2 Set 1	$\bar{\alpha}'_u$,[a] Å^2 Set 2	$n/2$[b] Set 1	$n/2$[b] Set 2
Au–Au str	3.45	3.04	0.088	0.076
Au–S str	2.78	2.98	0.236	0.254
C–S str	3.61	3.05	1.80	1.52
S–C–S bend	0.84	1.21	...	...

[a] Obtained with eq 1. The signs of $\bar{\alpha}'_{Q_i}$ were taken as $+ - - +$ (set 1) and $- - - +$ (set 2) for i = 1, 2, 3, 4, respectively. [b] Calculated using eq 2 with the following parameters: $Z_{Au} = 1$, $Z_S = 6$, $Z_C = 4$; $\chi_{Au} = 2.3$, $\chi_S = 2.5$, $\chi_C = 2.5$.

Discussion

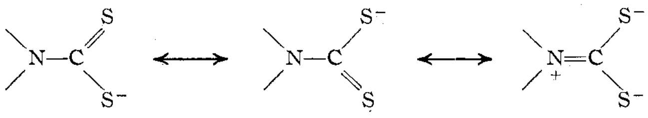
The chief point of interest in this study is to evaluate the extent of gold–gold interaction in $Au_2(S_2CN(C_4H_9)_2)_2$. This can be accomplished, at least semiquantitatively, with the aid of the δ function potential equation of Long and Plane,[16] which relates bond polarizability derivatives to bond orders

$$\bar{\alpha}'_u = \frac{2}{3}\frac{g\sigma}{Za_0}r^3\left(\frac{n}{2}\right) \qquad (2)$$

where n is the number of electrons in the bond, r is the bond length, a_0 is the Bohr radius, g is the δ function strength (taken as the square root of the Pauling electronegativity, χ), Z is the effective nuclear charge (taken as the atomic number minus the number of inner shell electrons), and σ is the Pauling covalent character[17] ($\sigma = \exp[-{}^1/_4(\chi_A - \chi_B)^2]$). For heteronuclear bonds the geometric mean of Z/g is taken.

The bond orders, $n/2$, calculated with eq 2 are not reliable in an absolute sense, but they show consistent behavior for chemically related species. It has been shown that $n/2$ falls in the range 0.3–0.4 for several nonbridged homonuclear metal–metal single bonds.[5] On the other hand for the bridged polynuclear complexes of Pt(IV), Bi(III), Pb(II), and Tl(I) mentioned in the Introduction, $n/2$ ranges[2] from 0.1 down to 0.02. For the Au–Au interaction in $Au_2(S_2CN(C_4H_9)_2)_2$, the values of $n/2$ obtained from the present result, 0.08 or 0.09 (Table VII), are in the latter range and well below the values typical for unequivocal metal–metal bonds.

Some speculation on the source of this weak metal–metal interaction may be in order. In their study of $Pt(S_2CHN_2)_2$ Nakamoto, *et al.*,[11] obtained a high C–N stretching force constant, 6.2 mdyn/Å, and suggested that among the three probable resonance forms of the dithiocarbamate ligand


I II III

form III, with a C–N double bond, is dominant. Our infrared spectrum shows a C–N stretching frequency, 1445 cm^{-1}, very close to those found in $Pt(S_2CNH_2)_2$, so that the same inference of C–N double bonding probably applies to $Au_2(S_2CN(C_4H_9)_2)_2$. Consistent with this, Hesse[9] found that the C_2NCS_2 unit is planar in the *n*-propyl analog of $Au_2(S_2CN(C_4H_9)_2)_2$. The extra charge separation in resonance form III is of course stabilized by the cation(s) to which the sulfur atoms are bound. By the same token form III promotes the transfer of charge from the sulfur atoms to the metal atom(s).

Two gold(I) ions would not ordinarily be expected to interact, except through charge repulsion, since their $5d^{10}$ valence state is reasonably stable. On the other hand, gold(0) atoms, with $5d^{10}6s$ valence state, interact strongly, as do the isoelectronic mercury(I) ions. The gas-phase dimer, Au_2^0, has a force constant[18] of 2.11 mdyn/Å, and the force constant for (aq)Hg_2^{2+} is 1.93 mdyn/Å.[19] It seems reasonble to think of the metal–metal interaction in $Au_2(S_2CN(C_4H_9)_2)_2$ as a consequence of charge transfer from the ligands to the gold(I) ions with the partial formation of a Au_2^0 bond. One can write resonance forms IV–VI.

The Raman intensity of Au_2^0 is unavailable. For the isoelectronic (aq)Hg_2^{2+}, however, $n/2 = 0.38$,[3] about four times the $(n/2)_{Au-Au}$ values found here. These results suggest that resonance forms such as V and VI contribute about 25% to the electronic structure of $Au_2(S_2CN(C_4H_9)_2)_2$. The present Au–Au force con-

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[14] R. E. Hester in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 4.

[15] D. A. Long, D. C. Milner, and A. G. Thomas, *Proc. Roy. Soc., Ser. A*, **237**, 197 (1956).

[16] T. V. Long, II, and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

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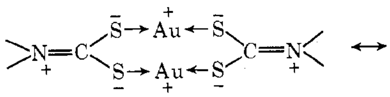
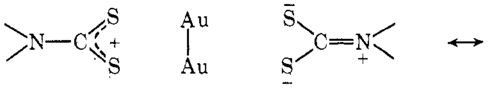
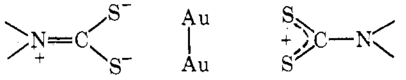
[19] H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, 616 (1966).



IV



V



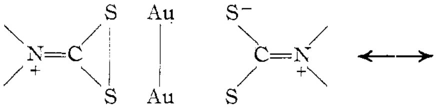
VI

stant, 1.95 mdyn/Å, is nearly as large as that of Au_2^0 and might have been taken to suggest a full Au–Au bond. However, force constants for cyclic molecules are not comparable with those for acyclic molecules, because of the extra redundancies among internal coordinates in the former. The Au–Au force constant in $Au_2(S_2CN(C_4H_9)_2)_2$ contains indeterminate contributions from ring angles which have been neglected in the normal-coordinate analysis: S–Au–Au and S–Au–S. It has previously been noted that metal–metal force constants in weakly interacting polynuclear complexes are much higher than the strength of the interaction would suggest.[2,3]

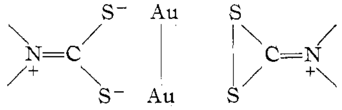
Contributions of resonance forms V and VI should also lower the bond order of the Au–S bonds below that expected for a mononuclear complex. Raman intensities for metal–sulfur bonds have not been previously reported, so there is no reference point for comparing the present $(n/2)_{\text{Au-S}}$ values, 0.24 or 0.25. For several metal–carbon bonds, $n/2$ ranges between 0.5 and 0.7.[2,4]

Because of the extensive mixing of C–S stretching and S–C–S bending, $\bar{\alpha}'_{\text{C-S}}$ and $\bar{\alpha}'_{\text{S-C-S}}$ are less well determined than $\bar{\alpha}'_{\text{Au-S}}$ and $\bar{\alpha}'_{\text{Au-Au}}$. In connection with the C–S bond order estimate, there is not much to choose between set 1 and set 2. Both suggest a bond order substantially in excess of unity. While the proposed 25% contribution from resonance forms V and VI would raise the theoretical C–S bond order to 1.12 and contributions from forms I and II would raise it slightly more, the $n/2$ values seem much too high, especially since they normally underestimate the theoretical bond order. For example $(n/2)_{\text{C-C}}$ in ethane is 0.5 or 0.7.[16] Excessive $n/2$ values have previously been found[20,21] in π-delocalized systems where coordinate mixing is extensive, a situation which obtains here. The effect has been ascribed to cooperative contributions to the molecular polarizability derivative, which are not taken into account in eq 1.

This effect may also explain the high $\bar{\alpha}'_{\text{S-C-S}}$ values reported here. In the Wolkenstein bond polarizability theory, bond bending is assumed not to contribute to molecular polarizability derivatives. Consistent with this assumption, measured values of $\bar{\alpha}'_{\text{bend}}$ have usually been quite small.[14] Values as high as 0.84 (set 1), let alone 1.21 (set 2), are unprecedented. Aside from the delocalization effect, such values might be taken to imply a degree of sulfur–sulfur interaction, since S–C–S bending is approximately equivalent to the stretching of a hypothetical S–S bond. Indeed it is not unreasonable to write the following resonance forms as alternatives to V and VI



VII



VIII

It must be admitted, however, that, in contrast to the Au–Au distance, the S–S distance, at 3.05 Å, gives no support for the idea of a bonding interaction. On the other hand, this distance is largely determined by the C–S bond length and the hybridization (sp^2) at the carbon atom.

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A Fluorine-19 Nuclear Magnetic Resonance Study of Some Boron Trifluoride Adducts

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Received July 16, 1970

A fluorine-19 nuclear magnetic resonance study of some substituted aromatic amine 1-oxide adducts of boron trifluoride was conducted. The $^{11}B-^{19}F$ spin–spin coupling constant is found to be negative in chloroacetonitrile. It is illustrated from the nmr data that variations in chemical shift are due primarily to steric factors.

Introduction

Inquiry into the $^{11}B-^{19}F$ spin–spin coupling constant in the tetrafluoroborate anion began several years ago with the studies of Kuhlman and Grant[2] and was later expanded by Gillespie and coworkers.[3] $J_{^{11}B-^{19}F}$ was

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