Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106

Kinetic Studies by NMR of Carbon–Nitrogen and Carbon–Oxygen Bond Rotations in Dithiocarbamate and Aryl Xanthate Complexes of Dimethylgold(III)

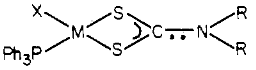
C. PAPARIZOS and J. P. FACKLER, JR.*

Received December 19, 1979

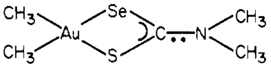
Dithiocarbamates and xanthates long have been known to show properties consistent with partial C$\underset{\cdot\cdot}{-}$N and C$\underset{\cdot\cdot}{-}$O double bonding. NMR studies with metal dithiocarbamates have concluded[1] that barriers to rotation about the C$\underset{\cdot\cdot}{-}$N bond are from 65 to 92 kJ mol^{-1}. Dimethylgold(III) dithiolates offer an unusual opportunity to evaluate these barrier energies by observation of the coalescence of ^{1}H or ^{13}C signals on the $(CH_3)_2Au$ portion of the molecule. Using the ^{1}H data, it has been possible to evaluate the C$\underset{\cdot\cdot}{-}$N barrier energy in $(CH_3)_2AuS_2CN(CH_3)C_6H_5$. $E_a \simeq 76 \pm 4$ kJ mol^{-1} in $CDCl_3$. The asymmetry induced at the $(CH_3)_2Au$ methyl positions by an aromatic ring over four bonds away is sufficient to enable the determination for the first time of the barrier to C$\underset{\cdot\cdot}{-}$O rotation in a metal xanthate, $(CH_3)_2AuS_2COC_6H_3(CH_3)_2$. $E_a \simeq 50 \pm 3$ kJ mol^{-1} in $CDCl_3$. The syntheses of these dimethylgold(III) dithiolates are described.

Introduction

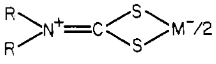
Molecular asymmetry centered on an atom located over 5 Å away from NMR active nuclei can induce magnetic nonequivalence.[1] With nickel triad complexes of type I (M = Pd(II), Pt(II); R = isobutyl; X = Cl$^-$, Br$^-$, I$^-$) magnetically nonequivalent alkyl groups are often observed at 100-MHz NMR frequencies in halohydrocarbon solvents. For the planar d^8 gold(III) complex II, Sonoda et al.[2] observed a small splitting (1–2 Hz at 90 MHz) for the CH_3Au protons and the CH_3N protons. The splitting for the CH_3N protons apparently arises from the restricted rotation about the C–N bond. In planar nickel triad dithiocarbamates, barriers to restricted rotation about the C$\underset{\cdot\cdot}{-}$N bond to $\Delta G^\ddagger$ (298 K) $\simeq$ 88 kJ/mol have been reported.[1] These barriers reflect the significant contribution of resonance form III to the description of these species.



I

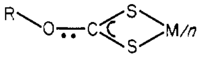


II



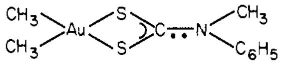
III

Xanthates IV also display some partial double-bond character[3] in the C$\underset{\cdot\cdot}{-}$O bond as measured by their IR spectra. However, prior to this work,[4] solution studies have failed to detect asymmetry in xanthates arising from restricted rotation about the C–O bond. Recently complexes have been synthesized[5] wherein R = aryl. These compounds show somewhat shorter S_2C–O distances than those of their alkyl analogues;[6] hence barriers to restricted rotation about C$\underset{\cdot\cdot}{-}$O are expected to be larger.

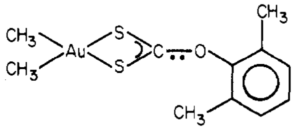


IV

Using the $(CH_3)_2Au$ as an NMR probe for molecular asymmetry, it has become possible to evaluate the kinetic parameters for C$\underset{\cdot\cdot}{-}$N and C$\underset{\cdot\cdot}{-}$O bond rotations in planar dimethylgold(III) dithiocarbamate (V) and dimethylgold(III) xanthate (VI) This paper describes the preparation of V and VI and the activation parameters for the hindered rotation about the C$\underset{\cdot\cdot}{-}$O and C$\underset{\cdot\cdot}{-}$N bonds in these compounds. These are the first studies to be reported of intramolecular rearrangement processes of gold(III) complexes which are rapid on the NMR time scale. Infrared spectra of the compounds were studied also, with special reference to the C$\underset{\cdot\cdot}{-}$O and C$\underset{\cdot\cdot}{-}$N stretching regions.



V



VI

Experimental Section

Physical Measurements. Nuclear magnetic resonance measurements were obtained on Varian A-60A and a Varian XL-100-V15 spectrometer equipped with a 620/L computer. The spectrometer was operated in the Fourier transform mode. Temperature regulation in the variable-temperature studies was done with the aid of a Varian V-6040 variable-temperature controller. The probe temperature was calibrated with ethylene glycol and methanol. An internal Me_4Si standard was used. Infrared spectra were recorded on a Beckman IR spectrophotometer with a range of 4000–625 cm^{-1}. The spectra were obtained by using KBr pellets (if solids) or neat liquids sandwiched between NaCl plates. Calibration was checked with polystyrene film. Melting points were determined on a laboratory device Mel-Temp melting point block and are reported uncorrected. Molecular weights were determined by using a Mechrolab vapor-phase osmometer calibrated with benzil.

A Univac 1108 computer equipped with a CALCOMP plotter was used for plotting purposes and line shape analyses.

Preparation of Compounds. All chemicals were used as purchased unless otherwise specified. Analyses were performed by Galbraith

---

(1) Fackler, J. P., Jr.; Lin, I. J. B.; Andrews, J. *Inorg. Chem.* **1977**, *16*, 450–457. Fackler, J. P., Jr.; Masters, A. F. *Inorg. Chim. Acta* **1980**, *39*, 113.

(2) Sonada, N.; Tanaka, T. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1145–1152.

(3) Chatt, J; Duncanson, A.; Venanzi, L. M. *Suom. Kemistil.* **1956**, *29*, 75. Davison, A.; Eges, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. McCormick, B. J. *Inorg. Chem.* **1968**, *7*, 1965–1970. Coucouvanis, D.; Fackler, J. P., Jr. *Ibid.* **1967**, *6*, 2047.

(4) A brief report of the restricted rotation in aryl xanthates is found in ref 5.

(5) Fackler, J. P., Jr.; Schussler, D. P.; Chen, H. W. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 27–42.

(6) Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 22–26.

0020-1669/80/1319-2886$01.00/0 © 1980 American Chemical Society

Table I. NMR Spectra of Dimethylgold(III) Complexes (Ppm)

	CH_3-Au	CH_3-N	CH_3	C_6H_5	OCH_2
	^1H NMR				
$(CH_3)_2AuS_2CN(CH_3)C_6H_5$	1.01^a	3.64^a		7.47^a	
	1.07^a				
	1.18^b	2.98^b		7.19^b	
	1.27^b				
	0.96^c	3.65^c		7.48^c	
$(CH_3)_2AuS_2CO(DMP)^{a,d}$	1.19		2.23	7.1	
$(CH_3)_2AuS_2COC_2H_5{}^a$	1.18		1.52		4.67
	^{13}C NMR				
$(CH_3)_2AuS_2CN(CH_3)C_6H_5{}^a$	5.51	42.06		126.94	
	5.3			129.22	
				130.15	
$(CH_3)_2AuS_2CO(DMP)^{a,d}$	5.67		16.11	127.20	
				128.90	
				130.40	
$(CH_3)_2AuS_2COC_2H_5{}^a$	5.87		13.69		69.52

[a] Using $CDCl_3$ as solvent; solutions are generally 0.5 M for ^1H and 1.0 M for ^{13}C. [b] Using C_6D_6 as solvent. [c] Using $C_6D_5NO_2$ as solvent; only one CH_3 resonance is observed. [d] DMP is 2,6-dimethylphenyl, $C_6H_3(CH_3)_2$.

Laboratories, Inc., Knoxville, Tenn.

Dimethyl(*N*,*N'*-methylphenyldithiocarbamato)gold(III). To a solution of[21] 0.215 g of $NaS_2CN(CH_3)(C_6H_5)$ in 10 mL of 1,4-dioxane was added a solution of[22] 0.36 g of $[(CH_3)_2AuI]_2$ in 5 mL of 1,4-dioxane slowly with stirring. A precipitate was obtained immediately (NaI). After filtration, the solvent was removed under vacuum. The orange residue was purified chromatographically (ethanol on silica gel). An orange-yellow solid was obtained which was soluble in most organic solvents; mp 67–69 °C. The ^1H and ^{13}C NMR values are given in Table I. Anal. Calcd for $C_{10}H_{14}NS_{14}NS_2Au$: C, 29.41; H, 3.43; S, 15.68. Found: C, 29.52; H, 3.51; S, 15.49. IR: 2990 (vw), 2905 (w), 1595 (m), 1515 (sh), 1502 (sh), 1485 (vs), 1473 (vs), 1395 (vs), 1272 (s), 1223 (s), 1195 (m), 1175 (m), 1115 (vw), 1080 (s), 1035 (w), 1011 (m), 975 (m), 850 (w), 800 (w), 780 (s), 708 (vs), 642 (s) cm^{-1}.

Dimethyl(2,6-dimethylphenyl xanthato)gold(III). To a THF solution of 0.3 g of potassium 2,6-dimethylphenyl xanthate[5] was added a solution of 0.2 g of[22] $[(CH_3)_2AuI]_2$ in 1,4-dioxane slowly with stirring under nitrogen. A precipitate was obtained. After filtration and evaporation under nitrogen, a yellow oily residue remained which was purified chromatographically (C_2H_5OH on silica gel). The product was a yellow liquid with a characteristic odor. The ^1H and ^{13}C NMR data are given in Table I. Anal. Calcd for $C_{11}H_{15}OS_2Au$: C, 31.2; H, 3.56. Found: C, 31.32; H, 3.61. IR: 3000 (vb), 2930 (m), 1480 (b, m), 1275 (m), 1240 (sh), 1220 (vs), 1205 (sh), 1150 (s), 1095 (vw), 1073 (s), 785 (m).

Dimethyl(ethyl xanthato)gold(III). To a suspension of potassium ethyl xanthate (0.29 g in 20 mL of THF) was added dimethylgold(III) iodide (0.5 g in 5 mL of THF) with stirring.[7] After filtration, vacuum evaporation produced a yellow residue which was purified chromatographically (ethanol on silica gel); mp 3–5 °C. ^1H and ^{13}C NMR data are given in Table I.

Nuclear Magnetic Resonance Techniques. Prior to solution preparation, $CDCl_3$, C_6D_6, $C_6H_5NO_2$, and C_6H_5Cl were deoxygenated by bubbling through dry N_2. The NMR spectra were recorded by techniques previously reported.[1]

Results

The ^1H and $^{13}C\{^1H\}$ NMR spectra of the two dimethylgold(III) complexes studied are presented in Table I. In $CDCl_3$ it is noted that both the ^1H and ^{13}C resonances of the CH_3Au are slightly more shielded (upfield) in the dithiocarbamate than in the xanthate. With $C_6D_5NO_2$ as a solvent, only one ^1H signal is observed for the CH_3Au unit in the dithiocarbamate complex.

At room temperature in $CDCl_3$ the dithiocarbamate complex V shows two equal intensity methyl resonances for the ^1H NMR of the $(CH_3)_2Au$ unit. When the temperature is increased, these lines coalesce (Figure 1). For the aryl xanthate VI two equal intensity methyl resonances are observed at temperatures below −60 °C (Figure 2).

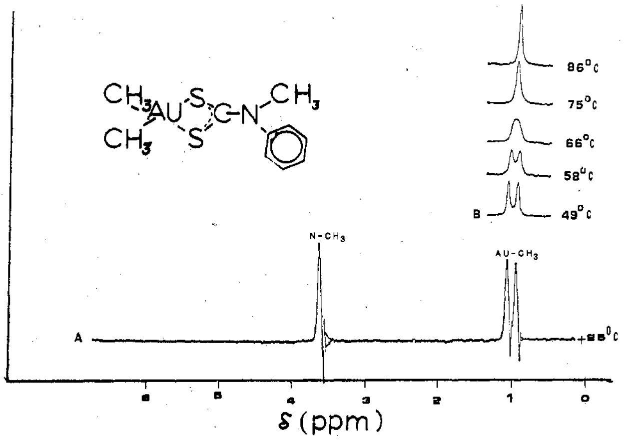


Figure 1. (A) ^1H NMR spectrum of $(CH_3)_2AuS_2CN(CH_3)C_6H_5$. (B) ^1H NMR spectra of the CH_3Au region at several temperatures.

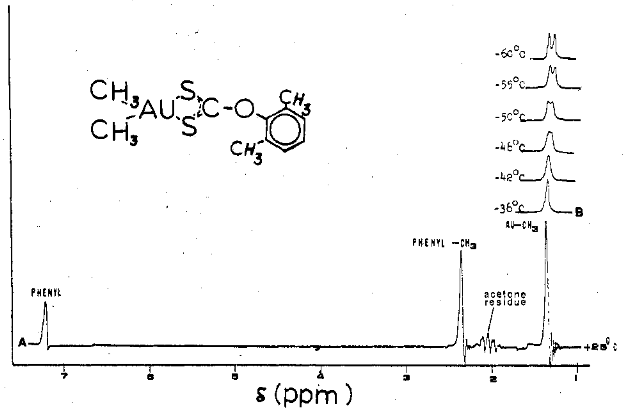


Figure 2. (A) ^1H NMR spectrum of $(CH_3)_2AuS_2CO(DMP)$. (B) ^1H NMR spectra of the CH_3Au region at several temperatures.

The ^1H NMR spectra[23] for the $(CH_3)_2Au$ unit can be treated as an exchange of methyl protons between two sites. The computer program[8] BINSCH DNMR3 was used to calculate the best value of $1/\tau$ at each temperature. This program is based on the equation for the NMR line shape as a function of exchange lifetime developed by Gutowsky, McCall, and Slichter.[9] The best fit to experimental line shapes were visually determined, and the resulting parameters at various temperatures were obtained. The rate constant, k (s^{-1}), is defined as $1/\tau$, where τ is the preexchange lifetime of a proton in either environment.

The activation energy for exchange was obtained by a linear plot of ln k vs. $1/T$, where the slope is $-E_a/R$. The kinetic parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined by the linear plot of $\ln (k/T)$ vs. $1/T$ in which the slope is $\Delta H^\ddagger/R$. The $\Delta G^\ddagger$ values can be calculated by the Eyring equation (1), where

$$k = \frac{1}{\tau} = K\,\frac{K_B T}{h}\exp\left(-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \qquad (1)$$

K is the transmission coefficient, assumed equal to 1, K_B is the Boltzmann constant, and h is Planck's constant. The values obtained are given in Table II. The experimental data used in these calculations are given.

---

(7) Bergfeld, M.; Schmidbaur, H. *Chem. Rev.* **1964**, *64*, 2306.

(8) Kleier, D. A.; Binsch, G. *QCPE* **1979**, *No. 165*. See ref 1 for details.

(9) Gutowsky, H. S.; McCall, D. W.; Schlichter, O. P. *J. Chem. Phys.* **1953**, *21*, 279.

Table II. Exchange Parameters for the C=N and C=O Bond Rotations in $CDCl_3$

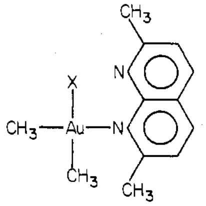
compd	T, °C	$1/\tau$, s^{-1}	parameters[a]
$Me_2AuS_2CN(CH_3)C_6H_5$	49	4.0	
	58	8.0	$E_a = 76 \pm 4$ kJ mol^{-1}
	66	16.0	$\Delta G^\ddagger = 72 \pm 4$ kJ mol^{-1}
	75	30.0	$\Delta H^\ddagger = 74 \pm 4$ kJ mol^{-1}
	86	70.0	$\Delta S^\ddagger = 2 \pm 4$ J mol^{-1} deg^{-1}
$Me_2AuS_2CO(2,5\text{-}Me_2C_6H_3)$	−60	2.0	
	−55	4.0	$E_a = 49 \pm 3$ kJ mol^{-1}
	−50	7.0	$\Delta G^\ddagger = 49 \pm 3$ kJ mol^{-1}
	−48	9.0	$\Delta H^\ddagger = 48 \pm 3$ kJ mol^{-1}
	−42	17.0	$\Delta S^\ddagger = 6 \pm 4$ J mol^{-1} deg^{-1}
	−38	27.0	

[a] $\Delta G^\ddagger$ at coalescence, 331 K for the dithiocarbamate and 223 K for the xanthate.

Discussion

Dimethylgold(III) complexes with halide or pseudohalide ligands occupying the remaining coordination positions about the gold generally have a cis planar AuC_2X_2 geometry, where X is halide or pseudohalide.[10] This geometry is common for other low-spin complexes of d^8 metal ions also. Intramolecular rearrangements of compounds containing the heavier $5d^8$ element ions such as Ir(I) or Pt(II) generally are slower than their $4d^8$ or $3d^8$ counterparts. With gold(III) very few complexes have been reported to be stereochemically nonrigid on the NMR time scale.

Elevated temperatures are usually required to cis $\rightleftharpoons$ trans isomerize[11] complexes such as $Me_2EtAuPPh_3$ wherein it is thought that a stereochemically nonrigid T-shaped three-coordinate intermediate, formed by dissociation of the phosphine, leads to the rearrangement. This isomerization is retarded by added phosphine. Schmidbaur and Dash,[12] however, have observed stereochemical nonrigidity of two types in 1,8-naphthyridine complexes of Me_2AuX, where X is a halide or pseudohalide, VII. The low-energy rearrangement equilibrates the methyl groups on the naphthyridine while the process which is observed in the NMR above 60 °C equilibrates the methyl groups on gold. This latter process involves pseudohalide exchange. Unfortunately only coalescence data were used to estimate $\Delta G^\ddagger$, which appears to be ~43 and ~71 kJ mol^{-1} for the two processes at the coalescence temperature of ~ −65 and ~30 °C, respectively.



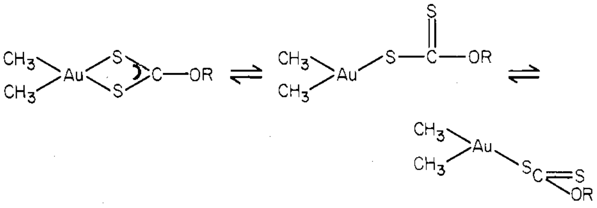
VII

For the 1,1-dithio complexes studied here there are several processes which may lead to the NMR equivalence of CH_3Au protons in these complexes. Among them are (1) exchange of methyl groups attached to gold, (2) dithiolate ligand exchange, (3) rotation about the >C=N and >C=O partial double bonds, and (4) multistep processes such as described below. At the temperature of coalescence the rate process was found to be concentration independent over a threefold dilution. This observation rules out any bimolecular process.

Tobias et al.[10] have studied the reaction of *cis*-$(CH_3)_2AuI(PR_3)$ with CD_3Li to produce *cis*-$(CH_3)_2CD_3AuPR_3$. They point out that there is no evidence for intramolecular exchange of methyl groups between positions cis and trans to the phosphine or for intermolecular exchange between $(CH_3)_2AuIPR_3$ molecules or between $(CH_3)_2CD_3AuPR_3$ and CD_3Li. These studies rule out methyl group exchange as a reasonable explanation for our NMR results.

When the temperature is increased or decreased, the CH_3N and CH_3Ph ^1H NMR signals are unchanged. They remain sharp over a range of temperatures between −50 and +85 °C. These results suggest that no dithiolate ligand exchange is observed on the NMR time scale.

Various multistep processes can be postulated which might lead to the observed magnetic equivalence of methyl groups on Me_2Au. One such process which must be considered is (2).



(2)

In this process it is assumed that the three-coordinate Me_2AuX unit has "T-shaped" stereochemical integrity. Kochi et al.[11] have postulated that a barrier exists between T-shaped configurations for monomeric R_3Au in order to explain kinetic results they have obtained. Molecular orbital calculations[14] suggest that the barrier to this rearrangement may be as large as 38 kJ mol^{-1}. The barriers we observe are considerably larger.

While multistep processes such as (2) have not been ruled out directly in this study, the results presented here are most consistent with interpretation based on hindered rotations about the C=N and C=O bonds. The following discussion assumes multistep processes are unlikely (see ref 15).

Examination of the data in Table II reveals that the $\Delta G^\ddagger$ for the C=N rotation is greater than that for C=O. It is known that the dithiocarbamate ligand can stabilize high oxidation states of metals. This behavior has been attributed to the lower electron-releasing ability of the −OR group compared to that of the $-NR_2$ group. The higher activation energy for C=N bond rotation reflects the increased multiple-bond character in the C=N bond compared with that of the C=O bond.

Binsch[16] has pointed out that the most accurate data for bond rotation are for the ones with small entropies of activation ($\Delta S^\ddagger$). Large negative values for $\Delta S^\ddagger$ have been interpreted to imply preferential solvation in the transition state.[16] The data we have obtained for $\Delta S^\ddagger$ are in the range of 2.5–5.7 (J deg^{-1} mol^{-1}), small enough to suggest that solvation effects are negligible.[15]

---

(10) Puddephatt, R. J. "The Chemistry of Gold"; Elsevier: Amsterdam, 1978 (recent review of gold chemistry).

(11) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; pp 269–278.

(12) Schmidbaur, H.; Dash, K. C. *J. Am. Chem. Soc.* **1973**, *95*, 4855.

(13) Shaw, C. F.; Tobias, R. S. *Inorg. Chem.* **1973**, *12*, 965.

(14) Komiya, S.; Albright, T. B.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

(15) A two-step mechanism involving a dissociative Au–S bond rupture followed by hindered stereochemical rearrangement (2) of the T-shaped intermediate is difficult to justify when one compares the relative $\Delta G^\ddagger$'s for the xanthate and dithiocarbamate complexes. The T-shaped intermediate would have the same metal–ligand coordination in both complexes. Yet the activation energy observed is nearly twice as large in the dithiocarbamate complex. A two-step mechanism should show a larger entropy of activation than we have observed. The $\Delta G^\ddagger$ values obtained here for C=N rotation are similar to activation energies observed for C=N rotations in other dithiocarbamate complexes. Finally, as Louw recently stated,[19] the dissociative two-step mechanism violates the 16–18-electron rule.

(16) Binsch, G. *Top. Stereochem.* **1968**, *3*, 97.

The $\Delta G^{\ddagger}$ values obtained here for the dithiocarbamate complex are similar to the $\Delta G^{\ddagger}$ values obtained by the restricted rotation in other bidentate dithiocarbamates.[1] The $\Delta S^{\ddagger}$ is somewhat more positive, however, in the Me_2Au complex than in Pd(II) or Pt(II) complexes studied previously, although no direct comparison can be made since different solvents were used. Nonetheless, the $\Delta S^{\ddagger}$ is considerably less positive than found (150 J deg^{-1} mol^{-1}) for the equilibration of SacSac methyl groups in Ni(SacSac)(PEt_3)Cl, a system wherein ligand dissociation is the most reasonable interpretation of the kinetic results.[1]

In contrast to the data with dimethyl(2,6-dimethylphenyl xanthato)gold(III), cooling a solution of dimethyl(*O*-ethyl xanthato)gold(III) in acetone-d_6 to −80 °C results in no broadening of the CH_3Au signals in the ^{1}H NMR spectrum. Structural data reveal that the $S_2C\overset{\cdots}{-}O$ distance for the aryl xanthates is shorter (1.30–1.33 Å) than that for the alkyl xanthates (1.38–1.39 Å). Hence the barrier to restricted rotation is expected to be smaller in the alkyl xanthates than in the aryl species. Restricted rotations about C–O bonds in sterically constrained aryl ethers have been reported.[17]

The absence of evidence for nonequivalent methyl groups to −80 °C in Me_2AuS_2COEt further mitigates against any multistep dissociative mechanism for the dynamic process. Assuming[20] a chemical shift behavior for the Me_2Au methyl groups similar to that observed in the static unsymmetrical dithiocarbamate complex, one concludes that the barrier to rotation about the $C\overset{\cdots}{-}O$ bond is less than 25 kJ mol^{-1} for the alkyl xanthate. A barrier this low is unreasonable for a multistep process which requires dissociative Au–S bond rupture.

The proton chemical shifts of $(CH_3)_2AuS_2CN(CH_3)C_6H_5$ are somewhat solvent dependent. In benzene-d_6, the $AuCH_3$ signals were shifted downfield, while the CH_3N and C_6H_5N signals were shifted upfield compared with the chemical shifts in CD_3Cl. The same behavior has been observed for Pd(S_2CNR_2)(PPh_3)Cl and $(CH_3)_2Au(XYCNEt_2)_2$ (X = S, Y = Se) complexes.[18] Specific solvation by the aromatic solvent appears to cause these effects with the planar molecules. In nitrobenzene-d_6 the CH_3Au protons become equivalent even at room temperature and are shifted upfield compared to their shift in benzene. The same results have been observed with dimethylformamide.

The IR spectra show bands near 1500 and 1250 cm^{-1}, respectively, as expected[24] for partial double-bond character in the $C\overset{\cdots}{-}N$ and $C\overset{\cdots}{-}O$ bonds. However, the phenyl ring vibrations obscure attempts to discuss these bands other than to point out their qualitative consistency with the high rotational barriers.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 76-18709, and the National Institutes of Health, Grant GM-19050.

Registry No. $(CH_3)_2AuS_2CN(CH_3)C_6H_5$, 74176-21-9; $(CH_3)_2AuS_2CO$(DMP), 74176-22-0; $(CH_3)_2AuS_2COC_2H_5$, 74176-23-1; $[(CH_3)_2AuI]_2$, 14951-47-4.

---

(17) Sternhell, S. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackson, L. N., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 191–194.

(18) Fackler, J. P.; Chan, L.-T.; Pan, W.-H.; Masters, A. F., to be submitted for publication.

(19) Louw, W. J. *Inorg. Chem.* **1977**, *16*, 2147.

(20) This assumption is weakened by the observation that both the aryl xanthate and the dithiocarbamate complexes contain aromatic groups capable of influencing the chemical shift differences of the two methyl groups more dramatically than is possible with only aliphatic components.

(21) Fackler, J. P., Jr. *Adv. Chem. Ser.* **1976**, *No. 150*, 394.

(22) Gibson, C. S.; Colles, W. M. *J. Chem. Soc.* **1931**, 2407.

(23) The chemical shift difference for the ^{13}C of the two methyl groups is observed but not used to evaluate kinetic data.

(24) Fackler, J. P., Jr.; Coucouvanis, D. *Inorg. Chem.* **1968**, *7*, 18.

Contribution from the Department of Chemistry,
Clarkson College of Technology, Potsdam, New York 13676

Resonance Raman Spectra of Bis, Planar Nickel(II)–Sulfur Ligand Complexes

O. SIIMAN

Received August 29, 1979

Resonance Raman (RR) spectra of $M^{II}S_2O_2$-core complexes, bis(thioacetylacetonato)nickel(II) and -palladium(II), and $Ni^{II}S_4$-core complexes, bis(dithioacetylacetonato)nickel(II), bis(1,2-diphenylethylene-1,2-dithiolato)nickel, and bis(1,2-dimethylethylene-1,2-dithiolato)nickel, were measured in the 1600–200-cm^{-1} region. In the oxygen-containing compounds excitation into charge-transfer electronic absorption bands between 550 and 400 nm produced RR enhancement, mainly, of ligand vibrations. On the other hand, excitation into charge-transfer bands of the $Ni^{II}S_4$ compounds gave RR intensification, predominantly, of nickel–sulfur vibrational modes. Use of Franck–Condon factors in correlating the types of modes of vibration that were RR enhanced and the nature of the electronic transition was made. Some revisions in vibrational mode and electronic absorption-band assignments are proposed.

Introduction

The position of first-row transition metal(II)–sulfur stretching frequencies, especially for Cu(II)–S bonds, has come under scrutiny[1] in connection with resonance Raman (RR) studies of metalloproteins. When copper thiolate compounds[2] in general are examined, a range of ν(Cu–S) frequencies, ~200–450 cm^{-1}, appears to be possible. Notwithstanding the effects of symmetry, this, at first sight, seemed to be an unusually wide range of frequencies for a metal–ligand vibration.

---

(1) (a) O. Siiman, N. M. Young, and P. R. Carey, *J. Am. Chem. Soc.*, **96**, 5583 (1974); (b) V. Miskowski, S.-P. W. Tang, T. G. Spiro, E. Shapiro, and T. H. Moss, *Biochemistry*, **14**, 1244 (1975); (c) O. Siiman, N. M. Young, and P. R. Carey, *J. Am. Chem. Soc.*, **98**, 744 (1976); (d) J. S. Thompson, T. J. Marks, and J. A. Ibers. *ibid.*, **101**, 4180 (1979); (e) O. Siiman and P. R. Carey, *J. Inorg. Biochem.*, **12**, 353 (1980).

(2) (a) N. S. Ferris, W. H. Woodruff, D. B. Rorabacher, T. E. Jones, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **100**, 5939 (1978); (b) A. Pignedoli and G. Peyronel, *Spectrochim. Acta, Part A*, **32A**, 1739 (1976); (c) G. C. Pellacani, G. Peyronel, and A. Pignedoli, *Gazz. Chim. Ital.*, **102**, 835 (1972).

0020-1669/80/1319-2889$01.00/0 © 1980 American Chemical Society