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 ^1H 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.

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(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.

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

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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.

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Table I. Electronic Absorption Bands (nm) and Proposed Assignments

NiL_2[b]		NiL'_2[c]		NiL''_2[d]	
630 (80)[a]	$d_{xz} \rightarrow d_{xy}$	672 sh (331)	$d_{x^2-y^2} \rightarrow d_{xy}$	901 (7950)	$b_{1u}\pi \rightarrow b_{2g}\pi^*$
513 (~1160)	$d_{z^2} \rightarrow d_{xy}$	552 (2818)	$d_{xz} \rightarrow a_u\pi^*$	641 sh (400)	$b_{1u}\pi \rightarrow d_{xy}$
477	$d_{xz} \rightarrow b_1\pi^*$	398 sh (4169)	$d_{yz} \rightarrow a_u\pi^*$	581 (720)	${}^{n}{=}S{:}^{e} \rightarrow b_{2g}\pi^*$
447 (~3300)	$d_{yz} \rightarrow b_1\pi^*$, $d_{xz} \rightarrow a_2\pi^*$			515 sh (1570)	${}^{n}{=}S{:}^{e} \rightarrow d_{xy}$
				481 (1900)	$a_u\pi \rightarrow b_{2g}\pi^*$
428	$d_{x^2-y^2} \rightarrow b_1\pi^*$				
418	$d_{yz} \rightarrow a_2\pi^*$				

[a] Molar extinction coefficients, ϵ, in parentheses. [b] From ref 3a. [c] From ref 3c. [d] From ref 4e. [e] Nonbonding (lone pair) sulfur orbital.

To lend support for these data, we have examined M(II)–S stretching frequencies with other metals. Toward this end we have used resonance Raman spectroscopy which promises to emerge as a powerful tool for the diagnosis of vibrational bands as well as electronic excited-state assignments in delocalized metal chelate ring systems. Herein, we assess the range of ν(Ni–S) with a variety of sulfur ligands (localized to highly delocalized pπ-bonding systems) and the possible appearance of resonance-enhanced ligand vibrations. RR spectra of the planar Ni(II) complexes NiL_2, NiL'_2, and NiL''_2 (L = thioacetylacetonate, L′ = dithioacetylacetonate, and L″ = 1,2-diphenylethylene-1,2-dithiolate) were studied. Laser excitation into low-energy parity-allowed electronic transitions that arise from metal–sulfur ligand bonding have included metal → ligand (MLCT), ligand → metal (LMCT) charge transfer, and n(nonbonding) → π^* or metal electronic absorption bands.

Experimental Section

The nickel(II) complexes under study were prepared as described previously.[3] Purity of the compounds was considered satisfactory when previous melting points and infrared spectra were reproduced.

Raman spectra were recorded with a Jarrell-Ash 25-500 double monochromator with a Hammamatsu R500 photomultiplier tube for detection and Spectra-Physics Model 165 argon and krypton ion lasers for excitation. Solid samples were packed into a circular groove of a rotating stainless-steel cell and irradiated at an angle of ~45° to the surface of the sample and cell. Scattered light was collected at 90° to the incident laser beam. Spectral conditions are reported in the figure captions.

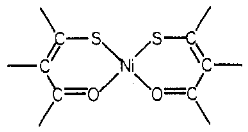
Results and Discussion

The electronic absorption spectra of NiL_2, NiL'_2, and NiL''_2 have previously been observed and analyzed. Relevant absorption-band maxima and their suggested assignments are summarized in Table I. Also, the infrared and regular Raman spectra of various monothioacetylacetonates and infrared spectra of dithioacetylacetonates and dithiolates have been analyzed by normal mode calculations. The results of previous vibrational and electronic spectral studies by us[3] and others[4] are used as a guide in the interpretation of RR spectra.

Thioacetylacetonate (L) Complexes. In Figure 1 are displayed the Raman spectra (A–D) of NiL_2, recorded with four exciting laser lines between 650 and 440 nm, as indicated in the caption. Analysis[3a] of the polarized 4 K single-crystal spectra of NiL_2 has suggested that bands between 550 and 440 nm be attributed to MLCT transitions (Table I). Therefore, spectra (B, C, and D in Figure 1) obtained by excitation at 514.5, 488.0, and 441.6 nm into allowed electronic absorption bands at 513, 477, and 447 nm can be expected to show the resonance Raman effect in some modes whereas spectrum A obtained by excitation at 647.1 nm into a low-intensity parity-forbidden d–d band at 630 nm is expected to resemble regular Raman spectra that were obtained with Zn(II), Cd(II),[3a,5] and Na(I)[6] complexes. The latter chelates show no electronic absorption bands with $\lambda_{max} > 400$ nm. The most intense high-frequency R bands occur at 1346 and 1469 cm^{-1} in ZnL_2, 1348 and 1504 cm^{-1} in CdL_2, and 1336 and 1488 cm^{-1} in NaL. Similarly, in metal acetylacetonates (AA) the most intense high-frequency R bands appear at 1373 and 1298 cm^{-1} in Al(AA)$_3$, 1375 and 1280 cm^{-1} in Ga(AA)$_3$, and 1373 and 1273 cm^{-1} in In(AA)$_3$. For the RR spectra of NiL_2 in Figure 1, however, changing the excitation wavelength from 647.1, 514.5, and 488.0 to 441.6 nm has the greatest effect on the relative intensity of the 1570-cm^{-1} band which becomes the most intense one with 441.6-nm excitation. This RR band is the highest frequency mode of NiL_2 in the non-C–H stretching frequency region and has an intense infrared counterpart[3a] at 1564 cm^{-1}. In normal Raman spectra of L complexes, it is a very weak band: 1590 cm^{-1} in ZnL_2, 1623 cm^{-1} in CdL_2, and 1610 cm^{-1} in NaL.

Normal-coordinate analyses[3a,6] that include deuterated derivative data of ML_2 and ML complexes and the SH protonated ligand, HL, indicated that this high-frequency band is assignable to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$. In the C_{2v} symmetry of NiL_2, the symmetric A_1 and asymmetric B_2 $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretching modes have about the same calculated frequency so that an intense infrared active $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ band was expected at the same frequency as the R and RR band. Isotope (^{13}C, ^{18}O) substitution work[8] with metal acetylacetonates also showed that the highest frequency band in the 1700–1200-cm^{-1} region was best assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$. This band is intense in the IR but very weak in R spectra. The most intense R band[7] between 1300 and 1250 cm^{-1} was assigned to $\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. The most intense Raman band of NiL_2 at 1470 cm^{-1} that is also assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ is resonance enhanced to a smaller degree than the 1570-cm^{-1} band. The other intense R band at 1360 cm^{-1} diminishes in relative intensity with excitation into the MLCT electronic absorption bands and has a R counterpart in acetylacetonates near 1373 cm^{-1}. It was assigned to the CH_3 symmetric deformation mode.

Vibrational and X-ray structural data have shown[3a] that bonding in the NiL_2 chelate rings most resembles the resonance structure



rather than the alternative form

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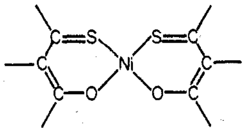
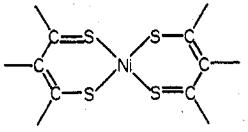


The C–S bond distance of 1.70 Å and stretching frequency of 721 cm^{-1} as well as shorter $(\text{C}\overset{\cdots}{-}\text{C})_s$ = 1.36 Å than $(\text{C}\overset{\cdots}{-}\text{C})_o$ = 1.41 Å bond distances agree with first structure. The RR spectra which show intensification of $\nu(\text{C}\overset{\cdots}{-}\text{O})$ and $\nu(\text{C}\overset{\cdots}{-}\text{C})_s$ also support this bonding arrangement. Since Ni(II) in metal complexes is not a readily reducible metal ion, Ni(II) (saturated thiolate ligand) complexes do not exhibit[9] the characteristic low-energy S → M charge-transfer electronic absorption bands that metal ions such as Cu(II) and Fe(III) do with sulfur ligands. The C–S bond of NiL_2 also shows very little π- bonding character so that the low-energy bands of NiL_2 that originate from MLCT transitions most probably involve antibonding π molecular orbitals over C and O atoms of the chelate ring as the electron sinks in the excited state. RR intensity[10] derived from allowed excited states has been associated with Franck–Condon overlaps[11] which are determined by force constant and bond distance changes between ground and excited states for bond stretching RR modes. The result of a d_π(Ni) → $L\pi^*$ transition is expected to perturb π(Ni–L) and π(L) bonding the most. Since S is involved in a minimal amount of π bonding with C, force constants and bond distances for $\text{C}\overset{\cdots}{-}\text{O}$, $\text{C}\overset{\cdots}{-}\text{C}$, Ni—O, and Ni—S might show the largest change. As only $\nu(\text{C}\overset{\cdots}{-}\text{O})$ and $\nu(\text{C}\overset{\cdots}{-}\text{C})$ are RR intensified significantly, we assume that occupation of the π^*L level in the excited state brings about the largest Franck–Condon effects. Similar RR results were observed with Fe(III) and Cu(II) transferrins[12] in which excitation into metal phenolate CT bands gave intense ligand RR bands but no observable intensity in metal–ligand modes.

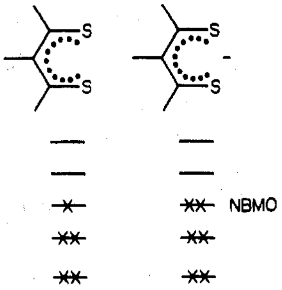
The palladium(II) analogue of the Ni(II) complex, PdL_2, presumbably has the same cis S,S structure as NiL_2 since the bis Pd(II) complex[13] with the β-diketone derivative, thiodibenzoylmethane, also exhibited the cis configuration. PdL_2 absorbs[4b,14] weakly near 535 nm (sh) but more strongly at 470 (sh) (ϵ 590) and 390 nm (ϵ 8680). The Raman spectrum shown in Figure 1, spectrum E for $Pd(TAA)_2$ with 514.5-nm excitation, indicates some preresonance enhancement of the 1580-cm^{-1} mode ($\nu(\text{C}\overset{\cdots}{-}\text{O})$) but resembles nonresonance $M(TAA)_2$ spectra at lower frequencies.

Dithioacetylacetonate (L′) Complexes. As illustrated in the Lewis structure of NiL'_2 and its resonance forms



$p\pi$(vertical) bonding appears to extend through C–S bonds. Extensive metal–ligand π bonding is reflected by the presence of intense low-energy electronic absorption bands[3c] in the visible spectra of ML'_2 chelates. The L′ ligand is an "odd" π-ligand system.[15] If attention is focused on the vertical π orbitals which tend to be the highest energy filled orbitals as well as the lowest energy empty ones, then Scheme I (a molecular orbital (MO) scheme) may be adopted. Odd ligand systems like L′ tend to exist as monoanions, L′$^-$, due to the presence of a singly occupied nonbonding π MO in its energy-level scheme and the absence of other low-lying π MOs to accept further electrons. With two ligands in NiL'_2, two occupied energy levels,[3c] one of b_{2g} and another of b_{1u} symmetry, have calculated energies in the same range as d-orbital energies. The L′ → M transitions, b_{2g} → b_{1g}(Ni) and b_{1u} → b_{1g}(Ni), are parity and symmetry forbidden, respectively, so that intense low-energy bands originating from LMCT transitions were not expected. MO calculations[3c] predicted, though, the presence of a π^* level of a_u symmetry (delocalized over S and C) and thus the appearance of a low-energy b_{2g} → a_u allowed M → π^*L′ transition. L′ complexes[3c,4c] all show a band between 16 000 and 22 000 cm^{-1} (ϵ ~2000–4000 M^{-1} cm^{-1}) that can be assigned to a MLCT band.

Scheme I



In Figure 2 are depicted the Raman spectra of NiL'_2 when 514.5- and 488.0-nm excitation (spectra D and E) into the 552-nm electronic adsorption band occurs. Though R spectra of ML'_2 complexes have not been recorded before, analyses[3b,4a] of IR spectra were performed for a 1:1 M:L′ model in C_{2v} symmetry. The simplified model is expected to be valid for higher frequency, mainly ligand-based, modes since very little coupling between the two chelate rings is expected for ligand backbone vibrations. However, low-frequency metal-sensitive modes of ML'_2 compounds are affected directly by the 1:1 M:L′ approximation. Since NiL'_2 belongs to the centrosymmetric point group, D_{2h}, the non-ν(C–H) Raman-active modes (7 A_g + 7 B_{1g}) and infrared-active modes (8 B_{2u} + 7 B_{3u}) are expected to be mutually exclusive.

The R spectra, in contrast to the IR spectrum of NiL'_2, do not exhibit characteristic C–CH_3 and C–H single-bond ligand-backbone vibrational bands nor non totally symmetric bands that were IR active. Resonance enhancement of selective symmetric modes by excitation into an allowed charge-transfer band are observed. MO calculations,[3c] which showed that σ bonding within the ligand did not have to be included to account for visible and near-UV electronic absorption bands, agree with the separation of σ-backbone bonding from chelate ring π-bonding effects. The RR bands (Figure 2, spectra D and E) are located at 367, 708, 1165, and 1355 cm^{-1} in order of decreasing intensity. Weak bands near 555 and 575 cm^{-1} were also detected. The most intense RR bands are expected to be assignable to chelate ring ν(Ni—S), $\nu(\text{C}\overset{\cdots}{-}\text{S})$, and $\nu(\text{C}\overset{\cdots}{-}\text{C})$ modes. For a $b_{2g}(\pi(\text{Ni,S,C,C'}))$ → $a_u(\pi(\text{S,C}))$ transition the largest Franck–Condon effects are anticipated in Ni—S, $\text{C}\overset{\cdots}{-}\text{S}$, and $\text{C}\overset{\cdots}{-}\text{C}$ bonds.

A similar situation was encountered with tetraphenyldithioimidodiphosphinate, L‴ = $(SPPh_2NPPh_2S)^-$, complexes. Excitation into a 585-nm CT band of Cu(II)L'''_2 and $Cu_3L'''_4$

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[14] O. Siiman, unpublished results.

[15] G. Schrauzer, *Acc. Chem. Res.*, **2**, 72 (1969).

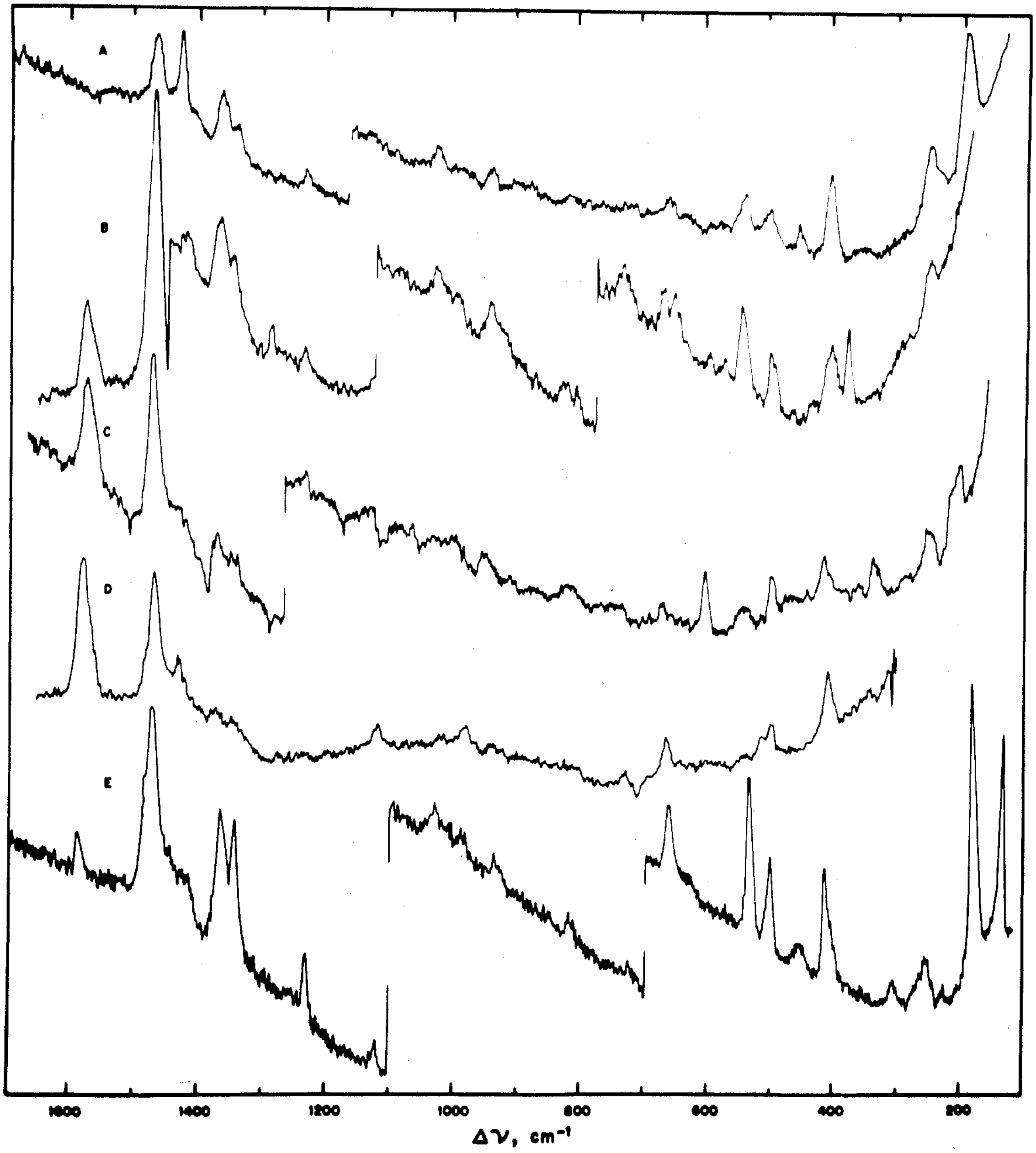

Figure 1. Resonance Raman spectra of solid bis(thioacetylacetonato)nickel(II) (A–D) and solid bis(thioacetylacetonato)palladium(II) (E). Experimental conditions (scan rate = 0.5 $\mathrm{cm^{-1}/s}$) are given (excitation, nm; power, mW; slit width, $\mathrm{cm^{-1}}$; sensitivity, counts/s; time constant, s). A: 647.1, $\mathrm{Kr^+}$; 120; 10.0; 1000; 5. B: 514.5, $\mathrm{Ar^+}$; 100; 10.0; 1000; 5. C: 488.0, $\mathrm{Ar^+}$; 80; 8.6; 800; 5. D: 441.6, Cd; 45; 10.0; 800; 2. E: 514.5, $\mathrm{Ar^+}$; 85; 7.0; 4000; 2.

gave intense RR bands[16] of chelate ring modes $\nu_s(\mathrm{P{\cdots}N{\cdots}P})$, $\nu_s(\mathrm{P{\cdots}S})$, and $\nu_s(\mathrm{Cu{-}S})$. The phenyl ring π system and P–C σ system were not electronically coupled to the chelate ring π system or Cu(II)–donor-atom σ system so that vibrational modes of side groups were not RR intensified.

When an allowed excited state is involved in RR studies, the symmetric stretching vibrations are the ones that couple most effectively[10] and are thus expected to be resonance enhanced. IR bands of $\mathrm{NiL'_2}$ at 371 and 390, 559, 705, 1158, and 1292 $\mathrm{cm^{-1}}$ were previously assigned[3b] to symmetric stretching modes ($\mathrm{A_1}$ species) $\nu(\mathrm{Ni{-}S})$, $\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{Ni{-}S})$, $\nu(\mathrm{C{\cdots}S})$, $\nu(\mathrm{C{-}CH_3})$, and $\nu(\mathrm{C{\cdots}C})$. Since the highest frequency non-C–H stretching fundamental of $\mathrm{NiL'_2}$ was the most intense IR band and was assigned to $\nu_{as}(\mathrm{C{\cdots}C{\cdots}C})$ at 1488 $\mathrm{cm^{-1}}$, we expect the highest frequency RR band at 1355 $\mathrm{cm^{-1}}$ to be ascribable to $\nu_s(\mathrm{C{\cdots}C{\cdots}C})$. Normal mode calculations[3b] based mainly on the assignment of the 1488-$\mathrm{cm^{-1}}$ IR band to $\nu_{as}(\mathrm{C{\cdots}C})$ gave calculated values of $\nu_{as}(\mathrm{C{\cdots}C}) = 1479\ \mathrm{cm^{-1}}$ and $\nu_s(\mathrm{C{\cdots}C}) = 1307\ \mathrm{cm^{-1}}$, which led us to believe that a 1292-$\mathrm{cm^{-1}}$ band was assignable to $\nu_s(\mathrm{C{\cdots}C})$. Increasing the force constant, $K(\mathrm{C{\cdots}C})$, should give a better fit for $\nu_{as}(\mathrm{C{\cdots}C})$ and put the calculated $\nu_s(\mathrm{C{\cdots}C})$ value closer to 1355 $\mathrm{cm^{-1}}$. In metal acetylacetonates (AA) the highly electronegative O atoms are expected to withdraw more electron density from the ring C atoms than do the less electronegative S atoms in metal dithioacetylacetonates. Higher $K(\mathrm{C{\cdots}C})$ and $\nu(\mathrm{C{\cdots}C})$ values, expected in $\mathrm{ML'_2}$ rather than M(AA) complexes, are reflected in relatively pure $\nu_s(\mathrm{C{\cdots}C})$ modes that were assigned to Raman bands at 1355 $\mathrm{cm^{-1}}$ in $\mathrm{ML'_2}$ and between 1250 and 1300 $\mathrm{cm^{-1}}$ in $\mathrm{M(AA)_3}$ complexes.[7] Previous assignment of $\delta(\mathrm{C{-}H})$ in $\mathrm{ML'_2}$ to the IR band at 1313 $\mathrm{cm^{-1}}$ agrees with $\mathrm{NiL_2}$ IR data[3a] (include γ-carbon deuterated species frequencies) that put

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[16] (a) O. Siiman, C. P. Huber, and M. L. Post, *Inorg. Chim. Acta*, **25**, L11 (1977); (b) O. Siiman and J. Vetuskey, *Inorg. Chem.*, **19**, 1672 (1980).

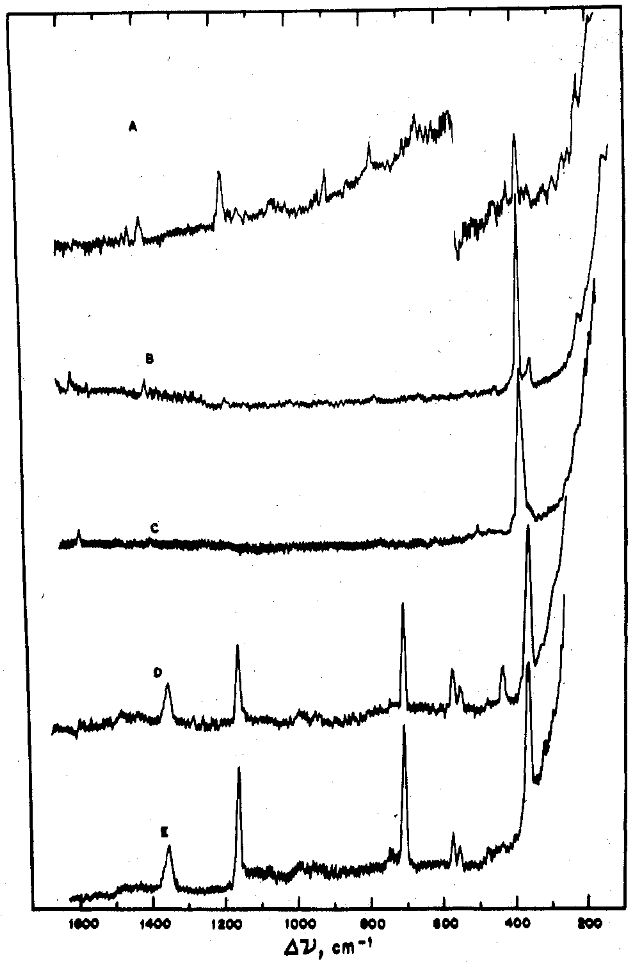
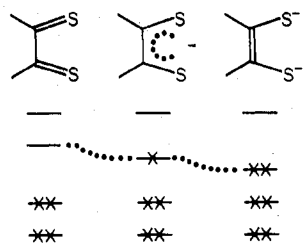


Figure 2. Resonance Raman spectra of solid bis(1,2-diphenylethylene-1,2-dithiolato)nickel (A–C) and solid bis(dithioacetylacetonato)nickel(II) (D and E). Experimental conditions (time constant = 5 s; scan rate = 0.5 cm^{-1}/s) are given (excitation, nm; power, mW; slit width, cm^{-1}; sensitivity, counts/s). A: 647.1, Kr^+; 150; 10.0; 1000. B: 514.5, Ar^+; 200; 8.6; 2000. C: 488.0, Ar^+; 200; 10.0; 2000. D: 514.5, Ar^+; 150; 10.0; 1000. E: 488.0, Ar^+; 200; 10.0; 1000.

δ(C—H) at 1338 cm^{-1}. The IR counterpart of the 1355-cm^{-1} RR band was previously assigned at 1352 cm^{-1} to a symmetric deformation of the methyl group. In $M(AA)_3$ both $\nu_s(C\overset{..}{-}C)$ and $\delta_s(CH_3)$ were observed as intense R bands.[7] Considering Franck–Condon effects related to NiL'_2 RR spectra and the non-RR enhancement of $\delta_s(CH_3)$ at 1371 cm^{-1} in NiL_2, we prefer to assign the 1292-cm^{-1} IR band, which has no RR counterpart, to $\delta_s(CH_3)$. Normal-coordinate calculations that associated IR bands at 1158, 705, 559, and 371 (but not 390) cm^{-1} with symmetric bond stretching modes are consistent with the observation of RR counterparts at 1165, 708, 555 and 575, and 367 cm^{-1}, respectively. Since ligand π bonding does not extend into the methyl groups, previous assignment of the 1158-cm^{-1} IR band solely to ν(C—CH_3) should be modified to account for the intense 1165-cm^{-1} RR band. In NiL_2 all R and RR bands in the 1300–700-cm^{-1} region, which might be linked with ν(C—CH_3), were very weak. As a chelate ring stretching mode frequency, 1165 cm^{-1} is too low for $\nu_s(C\overset{..}{-}C)$ but does fit into the range for $\nu_s(C\overset{..}{-}S)$. The 705-cm^{-1} IR band of NiL'_2 was assigned solely to $\nu(C\overset{..}{-}S)$ and, like $\nu(C\overset{..}{-}S)$ = 721 cm^{-1} in NiL'_2, is located at a similar frequency. A $\nu(C\overset{..}{-}S)$ assignment for the 708-cm^{-1} RR band is also suggested. As only one $\nu_s(C\overset{..}{-}S)$ normal mode is indicated for NiL'_2, we propose that extensive mixing of $C\overset{..}{-}S$ and C—CH_3 stretching modes is responsible for the presence of two intense RR bands in the 1300–700-cm^{-1} range. The contribution of $\nu(C\overset{..}{-}S)$ to a higher frequency fundamental at 1165 cm^{-1} in NiL'_2 suggests a greater degree of π delocalization in the L′ chelate ring system than in the L ring. A small contribution from a chelate ring mode, ν(Ni—S), to the proposed assignment, ν(C—CH_3) + ν(Ni—S), of an IR band near 559 cm^{-1} is in accord with the low intensity of two possible RR counterparts at 555 and 575 cm^{-1}. The main ν_s(Ni—S)-containing normal mode is linked with the highest intensity RR band at 367 cm^{-1} in the low-frequency region. Normal-coordinate analyses indicate that IR bands at 371 cm^{-1} in NiL'_2, 371 cm^{-1} in CoL'_2, 366 cm^{-1} in PdL'_2, and 371 cm^{-1} in PtL'_2 should be assigned to ν_s(M—S). Since the central metal atom does not move during a symmetric M—S stretching vibration of a planar MS_4 core with D_{2h} symmetry, the change in metal mass should cause ν_s(M—S) to shift very little compared to ν_{as}(M—S). The frequency difference, $\Delta = \nu_s - \nu_{as}$, may be taken[7] as a measure of relative M—S bond strengths. In brief, we have, in summarizing, IR[3b] and far-IR[5] data of ML'_2 complexes and RR data of NiL'_2. Pairs of stretching force constants K(Ni–S), K(Co—S) and K(Pd—S), K(Pt—S) should thereby be similar in value.

Scheme II



metal	ν_s, cm^{-1}	ν_{as}, cm^{-1}	Δ, cm^{-1}
Ni	367	288	79
Pd	366	254	112
Pt	371	264	107
Co	371	292	79

Dithiolate Complexes. Nickel(II) dithienes, $Ni(S_2C_2R_2)_2$ (R = H, CH_3, Ph) have a planar D_{2h} structure[17] similar to that of NiL'_2. Electronic[4e] and infrared[3d,4d] absorption spectra of metal dithienes have been reported and analyzed in previous work. Since four atoms (2 C, 2 S) of the dithiene ligand are part of the metal chelate rings, this ligand differs from L′ in that it is an "even" π-ligand system rather than an "odd" one. The π_V MO scheme[15] shows that the even ligand system can exist as a neutral ligand, monoanion, or dianion if the lowest unoccupied antibonding π MO is readily accessible. For neutral $Ni(S_2C_2R_2)_2$ complexes this scheme with two monoanion ligands leads[4e] to a high-energy filled π_V MO of b_{1u} symmetry and a low-energy empty antibonding $\pi_V{}^*$ MO of b_{2g} symmetry delocalized over the entire M–L system. The anticipation of a low-energy $b_{1u}(\pi) \rightarrow b_{2g}(\pi^*)$ transition materialized as an intense electronic absorption band in the 700–1000-nm range. The results of an MO calculation[4e] provide tentative assignments for other bands and are summarized in Table II.

NiL''_2, excited at 488.0 and 514.5 nm, showed (Figure 2, spectra C and B) a single intense RR band at 390 cm^{-1} and a weak band at 360 cm^{-1}. Excitation at 647.1 nm (Figure 2, spectrum A) gave major RR bands at 390 and 1178 cm^{-1} and some weak bands at 1400, 900, 780, 660, and 225 cm^{-1}. In none of these spectra were R bands of the phenyl groups observed. The methyl-for-phenyl-substituted compound, $Ni(S_2C_2(CH_3)_2)_2$, showed a similar intense RR band at 395

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[17] (a) D. Sartain annd M. R. Truter, *J. Chem. Soc. A*, 1264 (1967); (b) A. E. Smith, personal communication.

Table II. Resonance Raman Band Frequencies ($\mathrm{cm^{-1}}$) and Suggested Assignments

$\mathrm{NiL_2}$[a]		$\mathrm{NiL'_2}$[b]		$\mathrm{NiL''_2}$[c]		
				freq		
freq	assignt	freq	assignt	R = Ph	R = $\mathrm{CH_3}$	assignt
1570	$\nu_{A_1}(\mathrm{C\overset{\cdot\cdot}{-}O})$	1355	$\nu_{A_{1g}}(\mathrm{C\overset{\cdot\cdot}{-}C})$	1178		$\nu_{A_{1g}}(\mathrm{C\overset{\cdot\cdot}{-}S})$
1470	$\nu_{A_1}(\mathrm{C\overset{\cdot\cdot}{-}C})_s$	1165	$\nu_{A_{1g}}(\mathrm{C{-}CH_3}) + \nu_{A_{1g}}(\mathrm{C\overset{\cdot\cdot}{-}S})$	390	395	$\nu_{A_{1g}}(\mathrm{Ni{-}S})$
398	$\nu_{A_1}(\mathrm{Ni{-}O})$	708	$\nu_{A_{1g}}(\mathrm{C\overset{\cdot\cdot}{-}S}) + \nu_{A_{1g}}(\mathrm{C{-}CH_3})$	360		$\nu_{A_{1g}}(\mathrm{C{-}R}) + \nu_{A_{1g}}(\mathrm{C\overset{\cdot\cdot}{-}S}) + \nu_{A_{1g}}(\mathrm{Ni{-}S})$
241	$\nu_{A_1}(\mathrm{Ni{-}S})$	555, 575	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{Ni{-}S})$		305	$\delta_{A_{1g}}(\mathrm{C{-}CH_3}) + \nu_{A_{1g}}(\mathrm{Ni{-}S})$ or $\nu_{B_{3u}}(\mathrm{Ni{-}S})$
194	$\nu_{B_2}(\mathrm{Ni{-}S})$	367	$\nu_{A_{1g}}(\mathrm{Ni{-}S})$		200	ring def (A_{1g})
660, 641 (A_1, B_2)	$\delta(\mathrm{CCS}) + \delta(\mathrm{CCC}) + \delta(\mathrm{CCO})$					
536 (A_1)						
495 (B_2)						
371 (A_1, B_2)						
334 (A_1)						

[a] Assignments from ref 3a. [b] Assignments from ref 3b. [c] Assignments from ref 3d.

$\mathrm{cm^{-1}}$ with 488.0- and 514.5-nm irradiation. An additional medium-intensity band at 305 $\mathrm{cm^{-1}}$ appeared when the 514.5-nm but not when the 488.0-nm laser line was used. Another intense RR band was noted at 200 $\mathrm{cm^{-1}}$ with 488.0-nm but not 514.5-nm excitation.

In the 350–450-$\mathrm{cm^{-1}}$ region infrared spectra[3d,4d] of $\mathrm{Ni(S_2C_2R_2)_2}$ complexes contain only weak bands which may correspond to the 390-$\mathrm{cm^{-1}}$ RR band. Normal mode analyses[3d] offered assignments for $\nu_{B_{2u}}$(M–S) and $\nu_{B_{3u}}$(M–S) modes to IR bands in the 400–450- and 300–350-$\mathrm{cm^{-1}}$ ranges. Pd(II) and Pt(II) chelates of $\mathrm{S_2C_2(CH_3)_2}$ have more intense IR bands than the Ni(II) analogue in the 300–450-$\mathrm{cm^{-1}}$ region. The Pt(II) complex exhibits a distinct medium band near 402 $\mathrm{cm^{-1}}$ while the Pd(II) one absorbs at 385 $\mathrm{cm^{-1}}$.

None of the usual $\mathrm{CH_3}$ or Ph group vibrations were observed in the RR spectra of the $\mathrm{Ni(S_2C_2R_2)_2}$ complexes; thus, the chelate ring system, electronically uncoupled to side groups, can account for intensification of selective R bands by excitation into visible absorption bands. As in $\mathrm{NiL'_2}$, the 390-$\mathrm{cm^{-1}}$ low-frequency RR band is associated primarily with ν(Ni—S) rather than other chelate ring $\nu(\mathrm{C\overset{\cdot\cdot}{-}S})$ or $\nu(\mathrm{C\overset{\cdot\cdot}{-}C})$ modes. Again, ν_s(M—S) does not involve movement of the metal atom, so that ν_s(Pd—S) and ν_s(Pt—S) are expected to occur at frequencies similar to ν_s(Ni—S) unless M—S force constants vary greatly. IR bands of $\mathrm{Pt(S_2C_2(CH_3)_2)_2}$ at 402 $\mathrm{cm^{-1}}$ and $\mathrm{Pd(S_2C_2(CH_3)_2)_2}$ at 385 $\mathrm{cm^{-1}}$ and the RR band of $\mathrm{Ni(S_2C_2(CH_3)_2)_2}$ at 395 $\mathrm{cm^{-1}}$ conform to this expectation. Therefore, the latter bands are reasonably assigned to ν_s(M—S). Other observed RR bands are undoubtedly linked to normal modes which contain an Ni—S contribution. The 305-$\mathrm{cm^{-1}}$ RR band might be associated with a symmetric mode, which is predicted near 300 $\mathrm{cm^{-1}}$ for $\delta(\mathrm{C{-}CH_3})$ but which contains a substantial ν(Ni—S) part, or to an asymmetric ν(Ni—S) vibration. In $\mathrm{NiL'_2}$, ν_{as}(Ni—S) was predicted at 297 $\mathrm{cm^{-1}}$ and far-IR spectra showed a possible band assignment at 287 $\mathrm{cm^{-1}}$. The lowest frequency 200-$\mathrm{cm^{-1}}$ RR band might be assigned to a mode predicted as a symmetric in-plane chelate ring deformation at 205 $\mathrm{cm^{-1}}$. No other in-plane normal frequencies were calculated in this region. The absence of a $\nu(\mathrm{C\overset{\cdot\cdot}{-}S})$ RR band from excitation at 488.0 and 514.5 nm suggests that $\mathrm{C\overset{\cdot\cdot}{-}S}$ bonds are not significantly perturbed and, therefore, a L(π^*) level is not involved in the electronic transition to which the absorption band centered at 580 nm is assigned.[4e] An appropriate assignment for the 580-nm absorption band would be n(nonbonding sulfur) → Ni(II), in which case selective RR enhancement of Ni—S stretching vibrations is expected. Since excitation at 647.1 nm showed RR bands at 390 and 1178 $\mathrm{cm^{-1}}$, assignable to ν(Ni—S) and $\nu(\mathrm{C\overset{\cdot\cdot}{-}S})$ modes, and no RR activation of $\nu(\mathrm{C\overset{\cdot\cdot}{-}C})$ at 1358 $\mathrm{cm^{-1}}$ (infrared), the 640-nm electronic absorption band assignment[4e] of L(π) → Ni(II) is satisfactory provided the L(π) level is dominated by carbon-sulfur. Little enhancement of ν(Ni—S) band intensity is anticipated from the ligand-based $\pi \rightarrow \pi^*$ transition that has been assigned to the lower energy band at 900 nm. Presumably, resonance with the 900-nm band was not approached with excitation at 647.1 nm.

Conclusions

For the nickel complexes discussed herein, RR spectroscopy is shown to be a powerful tool for obtaining the energies of particular normal modes of vibration as well as gaining valuable information about the nature of electronic excited states. Of particular interest to us is the wide range of RR ν(Ni–S) frequencies that are possible for these chelates: 194, 241; 367; 390, 395 $\mathrm{cm^{-1}}$. The large intensity of low-energy visible absorption bands in some nickel complexes (dithioacetylacetonates and dithienes) can therefore be linked to higher Ni–S force constants and stronger metal–ligand bonds.

With association of the types of excited electronic absorption bands with RR enhancement of particular vibrational modes, implicit use of the Franck–Condon principle, which states that during the two photon RR scattering process the nuclei have not moved, has been made. The geometry of the molecule in the excited state is then instantaneously identical with that in the ground state. The molecule, therefore, rests momentarily in a geometrically strained state. The two factors (1) the magnitude of the difference in force constant(s) and (2) the magnitude of the difference in equilibrium bond distances and angles, for ground and excited states, that enter into Franck–Condon activation of particular normal modes of vibration cannot realistically be separated from each other. Knowledge of molecular excited states coupled with MO analyses are very helpful in predicting the types of normal modes that are resonance enhanced. Similar types of correlations have been made with electronic and RR spectra of π-delocalized organic compounds.[18]

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Registry No. Bis(thioacetylacetonato)nickel(II), 52612-96-1; bis(thioacetylacetonato)palladium(II), 16027-28-4; $\mathrm{Ni(S_2C_2R_2)}$, R = Ph, 28984-20-5; $\mathrm{Ni(S_2C_2R_2)}$, R = $\mathrm{CH_3}$, 38951-94-9; bis(dithioacetylacetonato)nickel(II), 10170-79-3.

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(18) Y. Nishimura, A. Y. Hirakawa, and M. Tsuboi, "Advances in Infrared and Raman Spectroscopy", Vol. 5, R. J. H. Clark and R. E. Hester, Eds., Heyden, New York, 1979, Chapter 4.