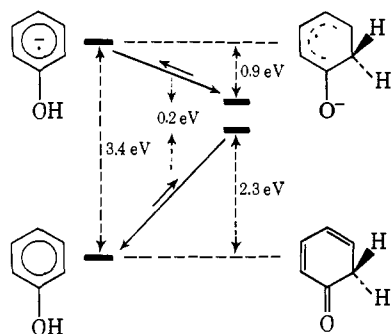As stated earlier, we proposed to attribute the observed reversal of the enol–keto tautomerism in the anionic state to the better electron-accepting capacity of the keto structure. Depicted in Chart I are the

Chart I

energetic relations between the enol and keto forms of phenol and their anions calculated by INDO molecular orbital theory.[8] The standard bond lengths and angles given in ref 8 were used for the calculation. Because of the uncertainties of the assumed structures, the exact energy differences given above should be viewed with some reservation. Nevertheless, the relative stabilities of the four species predicted by the theory are in excellent agreement with the experimental results.

The photoconversion of the anions of 2- and 4-pyridones (VIA and VIIIA) to their ketonic tautomers (VIB and VIIIB) is an interesting phenomenon since

the –NH– group is isoelectronic to $-CH_2-$. The greater stability of the keto forms may be attributed to their structural feature where both the oxygen and nitrogen atoms can share the anionic charge.

That 3-hydroxypyridine maintains the enol structure in its anionic state can also be attributed to a structural feature of the possible keto forms.

In these structures the negative charge of the anion cannot be imparted to the nitrogen atom. Perhaps in line with these observations, no significant energy difference (>0.2 eV) was predicted by INDO molecular orbital theory between the anions of the enol form (VII) and those of the keto structures shown above.

Finally, as we have reported earlier, the enamine–imine tautomerism of pyrrole is also reversed in its anionic state.[9]
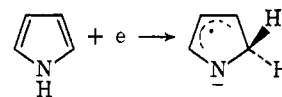
The similarity in the rationale of the reversal of tautomerism of pyrrole, phenols, and hydroxypyridines should be appreciated.

(9) Part II: P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **95**, 27 (1973).

Spectral Studies of Monothioacetylacetone and Its Sodium and Potassium Derivatives

Olavi Siiman, James Fresco, and Harry B. Gray*

Contribution No. 4799 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, and the Department of Chemistry, McGill University, Montreal, Quebec, Canada. Received July 19, 1973

Abstract: Infrared and Raman spectra of monothioacetylacetone and its dideuterio derivative recorded between 4000 and 200 cm^{-1} establish that the ligand exists predominantly in the thio–enol form. The infrared and Raman spectra of sodium and potassium monothioacetylacetonates, as solids and in solution, have been measured over the range 1700–100 cm^{-1}. A planar-chelated structural model for the alkali metal salts is proposed from vibrational assignments based on normal-coordinate calculations. The proton magnetic resonance spectra of solutions containing the sodium and potassium salts of monothioacetylacetonate show two sets of methyl and γ-proton signals, attributable to cis and trans isomers of monothioacetylacetonate. Conductance data establish that substantial ion pairing occurs in DMSO solutions between Na^+ or K^+ and monothioacetylacetonate, but because of very fast ligand substitution only a single set of pmr signals is observed for each geometrical isomer.

Although the vibrational and nuclear magnetic resonance spectra[1,2] of acetylacetone and alkali metal derivatives[3–5] of β-diketones have been studied

* Address correspondence to this author at California Institute of Technology.

(1) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

(2) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

(3) K. Shobatake and K. Nakamoto, *J. Chem. Phys.*, **49**, 4792 (1968).

(4) E. E. Ernstbrunner, *J. Chem. Soc. A*, 1558 (1970).

fairly extensively, the monothio analogs have not been similarly characterized. We have therefore analyzed the ir and Raman spectra of monothioacetylacetone (TAA) and both solids and solutions of the sodium and potassium salts of TAA⁻. Nmr spectra have been measured for TAA and solutions containing NaTAA and KTAA. To further characterize the properties of

(5) A. J. Carty, D. G. Tuck, and E. Bullock, *Can. J. Chem.*, **43**, 2559 (1965).
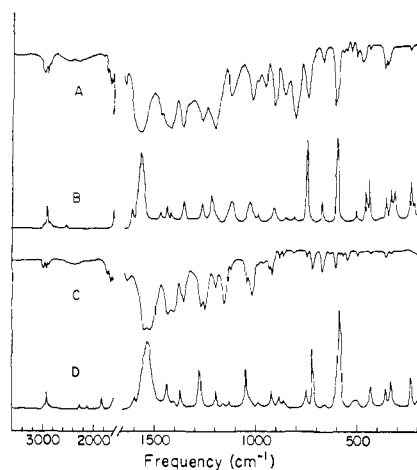
Figure 1. Infrared and Raman spectra of monothioacetylacetone (A, B) and monothioacetylacetone-d_2 (C, D): upper curves (A, C) are infrared absorbance *vs.* frequency; lower curves (B, D) are Raman intensity *vs.* frequency shift.

NaTAA and KTAA, conductance data have been obtained in DMSO solutions. These results and a discussion of their structural implications are presented herein.

Experimental Section

Monothioacetylacetonatosodium(I) was prepared by a previously reported method.[6] Monothioacetylacetonatopotassium(I) was prepared in an analogous manner. Acidification of monothioacetyl-acetonatosodium(I) with hydrochloric acid and deuterium chloride yielded monothioacetylacetone and monothioacetylacetone-d_2, respectively. The ligand was extracted from aqueous solution into a carbon tetrachloride phase, dried over anhydrous sodium sulfate, and concentrated. Exchange of the γ-proton of monothioacetyl-acetone with deuterium was enhanced by dissolving the sodium salt in a mixture of dimethyl-d_6 sulfoxide and deuterium oxide and shaking vigorously prior to acidification with deuterium chloride. Exchange >85% was verified by obtaining the proton magnetic resonance and mass spectra of monothioacetylacetone-d_2.

Monothioacetylacetonatopotassium(I) formed fine yellow crystals, mp >170° dec. *Anal.* Calcd for C_5H_7OSK: S, 20.78; K, 25.34. Found: S, 20.13; K, 24.44.

Monothioacetylacetone was obtained as a yellow liquid. A parent mass peak at 116 corresponds to that expected for C_5H_8OS: ^{1}H nmr spectrum (neat) $\delta_1(CH_3)$ 2.10, $\delta_2(CH_3)$ 2.38, $\delta(CH)$ 6.23, $\delta(S-H\cdots O)$ 13.48 ppm; intensity 3:3:1:1 (TMS = 0).

Infrared spectra were recorded with Perkin-Elmer Model 521, 225, and 301 spectrophotometers. Frequency readings were calibrated with polystyrene film and water vapor. The infrared spectra of liquids were obtained as neat samples between cesium iodide windows. Potassium bromide pellets and Nujol mulls were prepared for solids. Solution spectra were obtained between 1.0-mm path length barium fluoride and Teflon tape windows. Raman spectra of powdered solids, neat liquids, and deuterium oxide solutions in a 9.0-cm path length capillary were recorded with Jarrell-Ash 25-300 and Cary 81 spectrophotometers. The 647.1-nm Kr emission line of 0.39 W intensity and the 632.8 nm Ne line of 0.06 W intensity were used. Frequency shifts were calibrated with benzene and carbon tetrachloride.

Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer. Tetramethylsilane (TMS) was employed as an internal standard except for deuterium oxide solutions, where TMS was used as an external standard. Conductance measurements were performed at 25° with a Beckman Model KC 1632 conductivity bridge using a cell with 1-cm² platinum electrodes. The cell constant was determined by measuring the conductance of standard aqueous potassium chloride solutions. Spectrograde dimethyl sulfoxide was further purified by refluxing with calcium oxide for 4 hr prior to distilling under vacuum. The middle fraction with a resistance $>10^6$ Ω was used.

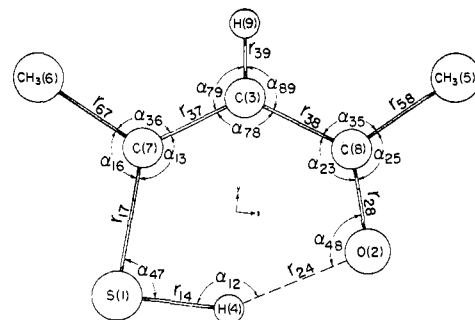(6) O. Siiman and J. Fresco, *J. Chem. Phys.*, **54**, 734 (1971).

Figure 2. Molecular structural model for monothioacetylacetone.

Results and Discussion

Infrared and Raman Spectra. Monothioacetylacetone and Monothioacetylacetone-d_2. The infrared and Raman spectra of TAA and TAA-d_2 are shown in Figure 1. The band located at 2540 cm^{-1} in the Raman spectrum of TAA occurs very weakly in the infrared and disappears in the spectra of the dideuterio species, being replaced by a Raman band at 1841 cm^{-1}. For the enol form of acetylacetone (shown[7] to have a planar ring and a linear, symmetrical hydrogen bond), the O-H stretch at 2750 cm^{-1} is shifted to 2020 cm^{-1} on deuteration.[1] Although the isotope shifts are similar, the frequencies are 200 cm^{-1} lower in the sulfur-containing ligand. Thus it is reasonable to attribute the 2540-cm^{-1} band in TAA to S-H stretching, as the position is in agreement with ν(S-H) for other thiols. In methyl mercaptan, ν(S-H) is found at 2597 cm^{-1},[8] whereas a band at 2450 cm^{-1} in dithiotropolone, which shifts to 1725 cm^{-1} in the monodeuterio species, has been assigned to S-H stretching.[9]

The hydrogen-bonded O$\cdots$H stretching vibration has been assigned to the band at 230 cm^{-1} in acetyl-acetone.[1] In TAA a similar absorption band appears at 237 cm^{-1} and shifts to 234 cm^{-1} in TAA-d_2. Infrared bands that have been identified with ν(C$\doteq$O) and ν(C-S) in M(TAA)$_2$ complexes[6] are located in the ranges 1610–1550 and 750–680 cm^{-1}, respectively. In TAA the C$\doteq$O and C-S stretching vibrations may be assigned to bands at 1610 and 745 cm^{-1}. Corresponding bands occur at 1598 and 722 cm^{-1} in TAA-d_2. The relative change in ν(C-S) upon deuteration is much larger than the change in ν(C$\doteq$O); therefore, the proton most probably resides closer to sulfur than oxygen in TAA. Weak bands that occur at 1715, 1662, and 1634 cm^{-1} in the ir spectra of TAA and TAA-d_2 suggest the presence of a small amount (<5%) of thioketo tautomer.[10]

A normal-coordinate analysis similar to the one performed for M(TAA)$_2$ complexes[6] was carried out, adopting a planar, nine-atom model (Figure 2). Except

(7) A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *J. Amer. Chem. Soc.*, **93**, 6399 (1971).

(8) R. E. Dininny and E. L. Pace, *J. Chem. Phys.*, **31**, 1630 (1959).

(9) C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 2297 (1970).

(10) Acetylacetone as a neat liquid is about a 5:1 mixture of enol-keto tautomers at room temperature (25°) and its pmr spectrum[2] shows both forms. The enol form exhibits a single methyl peak, indicating rapid hydrogen exchange between the two oxygen atoms. No thioketo form has been detected in the pmr spectrum of monothioacetylacetone, which has peaks at 13.48, 6.23, 2.38, and 2.10 ppm with an intensity ratio 1:1:3:3 for the pure liquid. Only the two methyl and one vinyl proton signals were detected down to temperatures of $-33°$ in CCl$_4$. However, a very small amount (<3%) of thioketo tautomer would escape detection in the pmr experiment.

Table I. Geometric Parameters for Monothioacetylacetone

$r_{17} = 1.83$ Å	$r_{28} = 1.26$ Å
$r_{14} = 1.35$ Å	$r_{24} = 1.80$ Å
$r_{37} = 1.36$ Å	$r_{67} = 1.51$ Å
$r_{38} = 1.41$ Å	$r_{58} = 1.51$ Å
	$r_{39} = 0.90$ Å
$\alpha_{13} = 126.5°$	
$\alpha_{78} = 127.0°$	$\alpha_{16} = 114.2°$
$\alpha_{32} = 125.7°$	$\alpha_{63} = 119.2°$
$\alpha_{84} = 103.4°$	$\alpha_{25} = 115.6°$
$\alpha_{47} = 87.0°$	$\alpha_{79} = \alpha_{89} = 116.5°$

mode assignments are summarized for TAA and TAA-d_2 in Table II. Urey–Bradley force constants, stretching (K), bending (H), and repulsive (F), that best reproduce the observed frequencies and isotope shifts, are listed in Table III.

The C–S stretching force constant, 3.65 mdyn/Å, is higher than the value (3.30 mdyn/Å) obtained for Ni-$(TAA)_2$,[6] and the C⋯O force constant, 8.25 mdyn/Å, is also greater than that (7.40 mdyn/Å) for the nickel(II) complex. If metal–oxygen bonding in monothioacetyl-

Table II. Observed and Calculated Vibrational Frequencies (cm^{-1})

Monothioacetylacetone				Monothioacetylacetone-d_2			
Obsd				Obsd			
Ir	R	Calcd	Predominant modes	Ir	R	Calcd	Predominant modes
In-Plane Vibrations							
2990		2990	ν(C–H)	2260	2261	2203	ν(C–D)
2490	2540	2580	ν(S–H)		1841	1850	ν(S–D)
1600	1610	1610	ν(C⋯O)	(1600)	1598	1610	ν(C⋯O)
1565	1567	1554	ν(C⋯C)ₛ	1530	1530	1541	ν(C⋯C)ₛ
1262	1266	1302	δ(C–H)	1197	1198	1247	ν(C⋯C)ₒ + ν(C–CH₃)ₒ
1200	1220	1201	ν(C–CH₃)ₒ + ν(C⋯C)ₒ	1158	1160	1164	ν(C–CH₃)ₛ
1124	1118	1122	ν(C–CH₃)ₛ	928	920	950	ν(C–CH₃)ₒ,ₛ
910	911	903	ν(C–CH₃)ₒ	880	880	852	δ(C–D)
859	863	880	δ(CSH)	720	722	722	ν(C–S)
745	745	747	ν(C–S)	630	(620)	620	δ(CSD)
608	595	598	δ(CCC) + δ(CCS) + δ(CCO)	605	588	593	δ(CCC) + δ(CCS) + δ(CCO)
507	507	489	δ(C–CH₃)ₛ	497	508	486	δ(C–CH₃)ₛ
365	368	377	δ(C–CH₃)ₛ + δ(CCS) + δ(CCO)	355	360	374	δ(C–CH₃)ₛ + δ(CCS) + δ(CCO)
330	332	350	δ(CCS) + δ(CCO) + δ(C–CH₃)ₒ	330	330	349	δ(CCS) + δ(CCO) + δ(C–CH₃)ₒ
	237	237	ν(O⋯H)		234	233	ν(O⋯D)
Out-of-Plane and Methyl Group Vibrations							
2980							
2918			ν(C–H)	2100	2120		ν(C–D)
2845							
1420	1442		CH₃ deg def	1435	1438		CH₃ deg def
				1405	1405		
1358	1365		CH₃ sym def	1358	1372		CH₃ sym def
1022	1030		CH₃ rock	1042	1047		CH₃ rock
960				1017	1020		
804	810		π(C–H)		543		π(C–D)
					560		
670	677		Out-of-plane	673	665		Out-of-plane
440	434		Out-of-plane	432	432		Out-of-plane

Table III. Force Constants (mdyn/Å) for Monothioacetylacetone

K_1(C–S) = 3.65	H_1(CCS) = 0.33	F_1(C⋯S) = 0.60
K_2(C⋯O) = 8.25	H_2(CCO) = 0.28	F_2(C⋯O) = 0.50
K_3(C⋯C)ₛ = 6.00	H_3(CCCH₃)ₛ = 0.30	F_3(C⋯CH₃) = 0.40
K_4(C–CH₃)ₛ = 3.20	H_4(H₃CCS) = 0.35	F_4(H₃C⋯S) = 0.55
K_5(S–H) = 3.55	H_5(H₃CCO) = 0.33	F_5(H₃C⋯O) = 0.45
K_6(O⋯H) = 0.28	H_6(HSC) = 0.17	F_6(C⋯H) = 0.06
K_8(C⋯C)ₒ = 4.40	H_7(HOC) = 0.05	F_7(C⋯H) = 0.01
K_9(C–CH₃)ₒ = 3.65	H_8(SHO) = 0.02	F_8(O⋯S) = 0.11
	H_9(CCC) = 0.35	F_9(C⋯C) = 0.37
	H_{10}(CCH) = 0.15	F_{10}(C⋯H) = 0.38
	H_{11}(CCCH₃) = 0.30	F_{11}(C⋯CH₃) = 0.40

for C–S, bond distances and angles given in Table I for TAA were transferred from the X-ray structural data for Ni(TAA)₂.[11] The C–S, S–H, and O⋯H bond lengths were estimated from corresponding distances in methyl mercaptan[8] and the acetic acid dimer.[12] Only the 15 in-plane vibrations were analyzed. Observed and calculated frequencies together with vibrational

(11) O. Siiman, D. D. Titus, C. D. Cowman, J. Fresco, and H. B. Gray, *J. Amer. Chem. Soc.*, **96**, 2353 (1974).

(12) J. Karle and L. O. Brockway, *J. Amer. Chem. Soc.*, **66**, 574 (1944).

acetonates is considered stronger than O⋯H hydrogen bonding in TAA (K(M–O) > K(O⋯H)), then decreased K(C⋯O) values are to be expected in the metal chelate as long as the K(C–CH₃) and K(C⋯C)ₒ values remain equal in the ligand and the complex. In TAA the values K(C⋯C) = 4.40 mdyn/Å and K(C–CH₃) = 3.65 mdyn/Å for the carbon–carbon bonds adjacent to C⋯O are essentially the same as the corresponding K's, 4.40 and 3.60 mdyn/Å, for Ni(TAA)₂. The constants K(S–H) = 3.55 and K(O⋯H) = 0.28 mdyn/Å are in reasonably close agreement with the related constants in methyl mercaptan (3.86 mdyn/Å)[8] and in the acetic acid dimer (0.33 mdyn/Å).[13] As expected, K(S–H) is larger than metal–sulfur stretching force constants in the M(TAA)₂ complexes and the carbon–carbon constant, K(C⋯C)ₛ = 6.00 mdyn/Å, is greater than its counterpart (4.40 mdyn/Å) in Ni(TAA)₂.

In-plane bending vibrations of the S–H group and the C–H group of the γ-carbon atom are assigned to bands at 863 and 1266 cm^{-1}, respectively. Deuteration shifts these bands to 630 and 880 cm^{-1}. A similar change in

(13) T. Miyazawa and K. S. Pitzer, *J. Amer. Chem. Soc.*, **81**, 74 (1959).
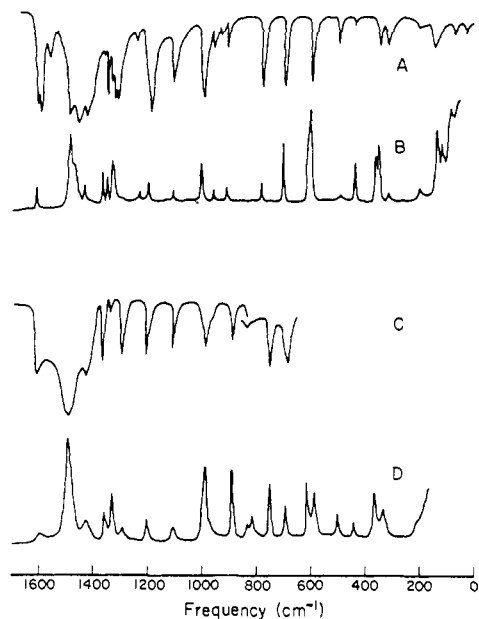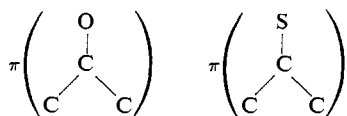
Figure 3. Infrared (A, dispersed in Nujol between CsI windows; C, in H_2O or D_2O solution between BaF_2 or Teflon tape windows) and Raman spectra (B, powdered solid; D, 5 M H_2O) of mono-thioacetylacetonatosodium(I).

the position of δ(C–H) = 1170 to δ(C–D) = 869 cm^{-1} was observed for the enol tautomer of acetylacetone.[1] The location of the bending vibration, δ(CSH) = 803 cm^{-1}, in methyl mercaptan[8] agrees closely with the related frequency (863 cm^{-1}) in TAA. The C–S stretching band occurs at 745 cm^{-1} in TAA; an analogous band in methyl mercaptan has been found[8] at 700 cm^{-1}. The force constants, K(S–H) = 4.30, K(C–S) = 3.86, and H(CSH) = 0.19 mdyn/Å, determined for methyl mercaptan,[8] are all larger than the corresponding constants (3.55, 3.65, and 0.17 mdyn/Å) for TAA.

The γ-C–H stretching frequency at 2990 cm^{-1} in TAA moves to 2260 cm^{-1} upon deuteration. The change is similar to the shift of the 2960 cm^{-1} fundamental to 2200 cm^{-1} in acetylacetone.[1] Evidently, some deuteration of the methyl hydrogen atoms occurs since a much weaker band at 2120 cm^{-1} is found in TAA-d_2.

The out-of-plane and methyl group vibrations have not been included in the normal-coordinate calculations but are assigned by comparison with their positions in compounds of similar composition and structure. The relative invariance of the band positions of CH_3 degenerate deformation, CH_3 symmetrical deformation, CH_3 rocking, and out-of-plane γ-C–H bending vibrations in monothioacetylacetonates,[6] acetylacetonates,[1] and dithioacetylacetonates[14] allows assignments of these fundamentals to be made. Finally, the bands at 670 and 440 cm^{-1} may be assigned tentatively to out-of-plane vibrations such as

$$\pi\left(\begin{array}{c} O \\ | \\ C \\ \diagup \quad \diagdown \\ C \quad\quad C \end{array}\right) \quad \pi\left(\begin{array}{c} S \\ | \\ C \\ \diagup \quad \diagdown \\ C \quad\quad C \end{array}\right)$$

Infrared and Raman Spectra. NaTAA and KTAA. The Raman spectra of NaTAA as a finely powdered

(14) O. Siiman and J. Fresco, *Inorg. Chem.*, **8**, 1846 (1969).

solid and as a 5 M deuterium oxide solution are shown in Figure 3. Also shown are the infrared spectra of NaTAA in a potassium bromide matrix and in water and deuterium oxide solutions. Comparison of the infrared spectra of NaTAA and M(TAA)$_2$ complexes[6] reveals close similarities. For example, absorption bands that have been assigned to ν(C$\doteq$O) at 1564 cm^{-1}, δ(C–H) + ν(C$\doteq$C) at 1476 cm^{-1}, ν(C$\doteq$C) + δ(C–H) at 1338 cm^{-1}, and ν(C–S) at 721 cm^{-1} in Ni-(TAA)$_2$ have counterparts at approximately 1601, 1460, 1325, and 706 cm^{-1} in NaTAA. The shift of the 1564-cm^{-1} band, which has been assigned to ν(C$\doteq$O) in Ni(TAA)$_2$ to 1601 cm^{-1} in NaTAA suggests a stronger carbon–oxygen bond and a weak Na$\cdots$O interaction in the latter case. To perform a normal-coordinate calculation analogous to the computation that was carried out for TAA, a 1 : 1 planar, (bidentate ligand)–metal model was assumed for NaTAA (a recent X-ray analysis of (1-phenylbutane-1,3-dionato)(ethylene glycol)sodium(I) has shown[15] similar chelation of sodium(I) by the benzoylacetonate anion). The Na–S and Na–O bond distances were estimated to be 2.50 and 2.25 Å, respectively. The remaining interatomic parameters were transferred from the X-ray structural results for Ni(TAA)$_2$.[11]

Inspection of the spectral data confirms that all normal vibrations are both infrared and Raman active. Assignments derived from a potential energy distribution for the in-plane vibrations are summarized in Table IV. The stretching, bending, and repulsive constants that best reproduce the observed frequencies are set out in Table V.

The solution infrared and Raman spectra of NaTAA exhibit a band at 753 cm^{-1}, which does not appear for the solid. The band becomes more intense in the Raman spectrum of NaTAA as an aqueous solution is diluted from 5 to 1 M. This band most likely is attributable to the carbon–sulfur stretching vibration in uncomplexed TAA$^-$, as the pmr spectra of NaTAA solutions confirm the presence of the anion (*vide infra*). The Raman band at 788 cm^{-1}, assigned to π(C–H) in solid NaTAA, splits into two bands, at 828 and 845 cm^{-1}, in NaTAA solutions. Frequency shifts for bands assigned to ν(C$\doteq$O), ν(C$\doteq$C) + δ(C–H), and ν(C–S) can be detected between solid and solution infrared and Raman spectra of NaTAA: for solid NaTAA, these bands are located respectively at 1610, 1332, and 706 cm^{-1}; in 5 M deuterium oxide solution, the bands shift to 1608, 1295, and 686 cm^{-1}.

The Na–O and Na–S stretching vibrations are provisionally assigned to bands at 158 and 100 cm^{-1}, respectively. The diminished force constants, K(Na–O) = 0.10 and K(Na–S) = 0.04 mdyn/Å, indicate weak interaction between Na$^+$ and the ligand donor atoms. Absorption bands that are located at 607, 510, 450, 360, and 330 cm^{-1} in NaTAA show little dependence on the metal ion, as they fall at 610, 502, 445, 368, and 320 cm^{-1} in KTAA. In addition, these bands are not shifted very far from their locations (595, 507, 440, 368, and 332 cm^{-1}) in TAA itself.

Assignments of the infrared and Raman bands of solid KTAA are given in Table VI. Band positions between 1700 and 300 cm^{-1} in KTAA and NaTAA

(15) D. Bright, A. J. Kolombos, G. H. W. Milburn, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc. D*, **49** (1970).

Table IV. Observed and Calculated Vibrational Frequencies (cm^{-1}) for Monothioacetylacetonatosodium(I)

Solid		D$_2$O and H$_2$O soln			
Ir	R	Ir	R	Calcd	Predominant modes
					In-Plane Vibrations
1610	1610	1608	1603	1591	ν(C$\cdots$O)
1600					
1496	1488	1495	1498	1502	δ(C–H) + ν(C$\cdots$C)
1460	1477				
1332	1336	1340	1337	1337	ν(C$\cdots$C) + δ(C—H)
1320	1330	1295	1296		
1198	1202	1210	1217	1210	ν(C–CH$_3$) + ν(C$\cdots$C)
1115	1117	1110	1113	1126	ν(C–CH$_3$)
			1100		
918	919	892	896	912	ν(C–CH$_3$)
706	708	754	753	717	ν(C–S)
		686	697		
607	618		678	593	δ(CCC) + δ(CCS) + δ(CCO)
	608		588		
510	503		505	491	δ(C–CH$_3$)
360	362		368	365	δ(C–CH$_3$) + δ(CCS) + δ(CCO)
330	325		335	335	δ(C–CH$_3$) + δ(CCS) + δ(CCO)
214	212			216	δ(ONaS) + δ(NaOC) + δ(NaSC)
158	152			160	ν(Na–O)
90	100			108	ν(Na–S)
					Out-of-Plane and Methyl Group Vibrations
1430	1434	1430	1430		CH$_3$ deg def
1354	1355	1368	1362		CH$_3$ sym def
	1368				
1003	1009	990	992		CH$_3$ rock
965	968	968	960		
784	788	838	845		π(C–H)
			828		
450	450		455		Out-of-plane

Table V. Force Constants (mdyn/Å) for NaTAA

K_2(C–S) = 3.00	H_1(CCS) = 0.23	F_1(C$\cdots$S) = 0.55
K_2(C$\cdots$O) = 8.00	H_2(CCO) = 0.26	F_2(C$\cdots$O) = 0.50
K_3(C$\cdots$C)$_s$ = 4.60	H_3(CCCH$_3$)$_s$ = 0.25	F_3(C$\cdots$CH$_3$) = 0.40
K_4(C–CH$_3$)$_s$ = 3.60	H_4(H$_3$CCS) = 0.35	F_4(H$_3$C$\cdots$S) = 0.60
K_5(Na–S) = 0.04	H_5(H$_3$CCO) = 0.33	F_5(H$_3$C$\cdots$O) = 0.45
K_6(Na–O) = 0.10	H_6(NaSC) = 0.05	F_6(Na$\cdots$C) = 0.06
K_8(C–C)$_o$ = 4.40	H_7(NaOC) = 0.06	F_7(Na$\cdots$C) = 0.06
K_9(C–CH$_3$)$_o$ = 3.60	H_8(SNaO) = 0.08	F_8(O$\cdots$S) = 0.08
	H_9(CCC) = 0.38	F_9(C$\cdots$C) = 0.37
	H_{10}(CCH) = 0.18	F_{10}(C$\cdots$H) = 0.50
	H_{11}(CCCH$_3$)$_o$ = 0.25	F_{11}(C$\cdots$CH$_3$) = 0.40

appear to be nearly identical. The 214-cm^{-1} band in NaTAA does move to 205 cm^{-1} in KTAA; it is assigned to the bending vibration, δ(OMS) + δ(MOC) + δ(MSC). No bands between 90 and 200 cm^{-1} were found for KTAA; therefore, ν(K–O) and ν(K–S) apparently occur below 90 cm^{-1}.

Pmr Spectra and Conductance Data. Proton chemical shifts for diamagnetic bischelates of acetylacetonate (AA$^-$),[16] TAA$^-$,[6] and dithioacetylacetonate (DTAA$^-$)[14] are summarized in Table VII. Although the positions of pmr signals are not very sensitive to the nature of the metal, the successive substitution of sulfur for oxygen significantly affects chemical shifts. The γ-proton signal is most sensitive; it is shifted to low field stepwise by about 1 ppm from $\sim$5.5 ppm in M(AA)$_2$ to

(16) R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).

Table VI. Infrared and Raman Spectral Data (cm^{-1}) for KTAA

Infrared	Raman	Predominant modes
		In-Plane Vibrations
1620	1605	ν(C$=$O)
1600		
1480	1468	δ(C–H) + ν(C$\cdots$C)
1328	1336	ν(C$\cdots$C) + δ(C–H)
1207	1209	ν(C–CH$_3$) + ν(C$\cdots$C)
1104	1110	ν(C–CH$_3$)
918	920	ν(C–CH$_3$)
708	712	ν(C–S)
610	616	δ(CCC) + δ(CCS) + δ(CCO)
502	504	δ(C–CH$_3$)
368	373	δ(C–CH$_3$) + δ(CCS) + δ(CCO)
320	322	δ(C–CH$_3$) + δ(CCS) + δ(CCO)
205	206	δ(OKS) + δ(KOC) + δ(KSC)
		Out-of-Plane and Methyl Group Vibrations
1428	1442	CH$_3$ deg def
1355	1358	CH$_3$ sym def
1000	1012	CH$_3$ rock
964		
779	784	π(C–H)
445	448	Out-of-plane

Table VII. Methyl and γ-Proton Resonances (in ppm Relative to TMS) of Metal Acetylacetonates (AA$^-$), Monothioacetylacetonates (TAA$^-$), and Dithioacetylacetonates (DTAA$^-$) in CDCl$_3$ Solutions at 25°

Metal	AA^{-a}		TAA^{-b}			DTAA^{-c}	
	δ(C–H)	δ(CH$_3$)	δ(C–H)	δ_2(CH$_3$)	δ_1(CH$_3$)	δ(C–H)	δ(CH$_3$)
Zn(II)	5.47	2.00	6.51	2.40	2.20		
Ni(II)			6.39	2.16	2.06	7.13	2.34
Pd(II)	5.42	2.07	6.44	2.37	2.25	7.18	2.52
Pt(II)	5.53	2.08					
Cd(II)			6.51	2.37	2.18		
Pb(II)			6.41	2.43	2.20		
Na(I)^d	4.86	1.65	6.26	2.53	1.83		
				2.22	2.05		
Na(I)^e	4.83	1.64	6.20	2.47	1.75		
			6.04	2.26	2.15		
K(I)^d	4.72	1.72	6.31	2.53	1.85		
			6.19	2.20	2.20		
K(I)^e	4.67	1.73	6.23	2.50	1.79		
			6.06	2.33	2.17		

^{a} From ref 16. ^{b} From ref 6. ^{c} From ref 14. ^{d} This work; in 4.0 M DMSO-d_6 solution. ^{e} This work; in 1.0 M DMSO-d_6 solution.

$\sim$6.4 ppm in M(TAA)$_2$ to $\sim$7.2 ppm in M(DTAA)$_2$. On the other hand, the methyl proton chemical shifts in acetylacetones and dithioacetylacetonates differ by only about 0.5 ppm. The chemical shift of $\sim$2.0 ppm for methyl protons near oxygen atoms in M(AA)$_2$, as contrasted to a value of $\sim$2.5 ppm for methyl protons near sulfur atoms in M(DTAA)$_2$, suggests that δ_1(CH$_3$) and δ_2(CH$_3$) in M(TAA)$_2$ originate from methyl protons near carbon–oxygen and carbon–sulfur bonds, respectively.

The pmr spectra of NaTAA and KTAA were studied in several solvents. The concentration dependence of the pmr spectra of NaTAA in dimethyl-d_6 sulfoxide is shown in Figure 4. A DMSO-d_6 solution 5 M in NaTAA exhibits a single γ-proton peak and four peaks due to methyl groups. Upon dilution there appear two γ-proton signals, in addition to the four methyl proton signals. The intensities of peaks at 2.19 and 2.05 ppm in 5 M solution relative to peaks at 2.53 and 1.83 ppm decrease about twofold in 2 M solution. In 0.1 M solution the middle two peaks at 2.26 and 2.15 ppm
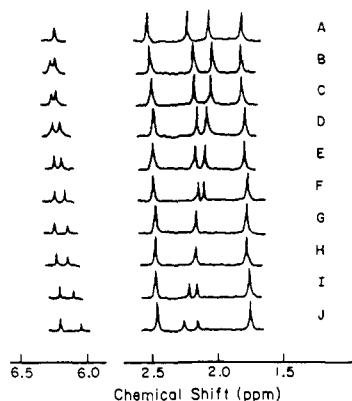
Figure 4. ¹H nmr spectra of NaTAA in DMSO-d_6: A, 5.0; B, 4.5; C, 3.5; D, 2.5; E, 2.0; F, 1.5; G, 1.0; H, 0.8; I, 0.5; J, 0.25 M.
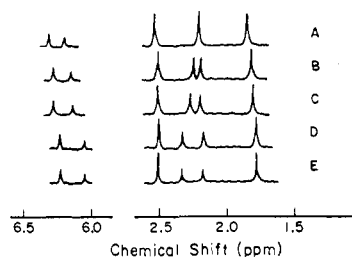

Figure 5. ¹H nmr spectra of KTAA in DMSO-d_6: A, 4.5; B, 3.0; C, 2.5; D, 1.5; E, 1.0 M.

almost disappear. The positions of the methyl and vinyl proton signals also change with decreasing concentration. The peak at 2.19 ppm in 5 M solution moves to high field (2.18 ppm, 1.5 M; 2.17 ppm, 0.8 M; 2.15 ppm, 0.25 M), whereas the signal at 2.05 ppm in 5 M solution shifts to low field (2.11 ppm, 1.5 M; 2.17 ppm, 0.8 M; 2.26 ppm, 0.25 M). The methyl proton resonances at 2.53 and 1.83 ppm remain nearly invariant to changes in concentration. In addition, the γ-proton signal at 6.29 ppm in 4.5 M solution decreases to 6.20 ppm at 0.25 M, whereas the signal at 6.26 ppm in 4.5 M solution decreases to 6.04 at 0.25 M. The intensity of the high field peak relative to the low field signal drops from approximately 1:1 at 4.5 M to about 1:3 at 0.25 M.[17]

The pmr spectral changes in DMSO-d_6 solutions of KTAA due to concentration variation are similar to those found for the sodium salt (Figure 5). In a 4.5 M DMSO-d_6 solution of KTAA there are two vinyl proton signals (6.31, 6.19 ppm) and three methyl signals (2.20, 2.53, 1.85 ppm). This spectrum is analogous to ones for the sodium salt at 1.0 and 0.8 M. Upon dilution the methyl proton signal at 2.20 ppm splits into two, the positions of peaks at 2.53 and 1.85 ppm change very little, and the separation of the vinyl proton signals at 6.31 and 6.19 ppm increases slightly.

The conductances of DMSO solutions of NaTAA and KTAA were measured for concentrations between

(17) The temperature dependence of the pmr spectra of NaTAA solutions was found to be very small. For a 5 M DMSO-d_6 solution of NaTAA, no change was observed in the positions and intensities of the methyl proton signals in the range 25–75° (100 MHz spectrometer). The vinyl proton signals at 6.18 and 6.16 ppm at 25° move to 6.20 and 6.13 ppm at 75°. The only difference between pmr spectra of 1 M NaTAA in a 2:1 (molar) D₂O–DMSO-d_6 solution at 18 and −50° (220 MHz spectrometer) is a slight decrease (0.15–0.11 ppm) in the separation of the γ-proton signals at the lower temperature.
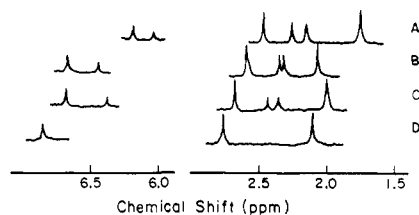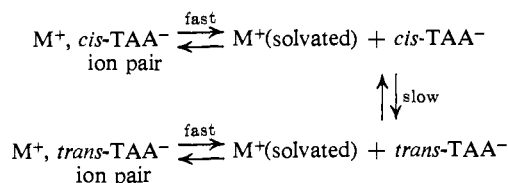

Figure 6. ¹H nmr spectra of NaTAA in 0.2 M solutions: A, DMSO-d_6; B, D₂O; C, methanol; D, pyridine.

Table VIII. Methyl and γ-Proton Resonances (in ppm Relative to TMS) of NaTAA in D₂O and Methanol Solutions at 25°

(NaTAA), M	δ(C–H)	δ_2(CH₃)	δ_1(CH₃)
	In D₂O		
5.0	6.62	2.57	2.06
	6.44	2.29	2.23
3.0	6.64	2.57	2.06
	6.45	2.30	2.27
1.0	6.67	2.59	2.07
	6.47	2.33	
0.5	6.67	2.59	2.07
	6.46	2.34	
0.25	6.67	2.59	2.07
	6.46	2.33	2.35
0.1	6.69	2.61	2.09
	6.48	2.34	2.37
	In CH₃OH		
1.6	6.68	2.68	2.01
	6.46	2.33	2.19
0.8	6.71	2.67	2.00
	6.45	2.34	2.29
0.3	6.68	2.66	1.99
	6.39	2.36	
0.2	6.69	2.68	2.00
	6.38	2.36	2.43

2.0 and 10⁻⁴ M at 25°. The equivalent conductances (Λ, in ohm⁻¹ cm²) increase as the concentrations decrease for NaTAA (6.9, 1.0 M; 22.7, 0.1 M; 40.0, 10⁻⁴M) and KTAA (9.8, 1.0 M; 26.0, 0.1 M; 375, 10⁻⁴M) in DMSO. The low molar conductances (<10 ohm⁻¹ cm²) obtained for solutions above 1 M establish that ion pairing is significant.

We suggest that the conductance and pmr data can be interpreted in terms of equilibria among ion pairs and anions of the types

$$\text{M}^+,\ cis\text{-TAA}^- \underset{\text{ion pair}}{\overset{\text{fast}}{\rightleftharpoons}} \text{M}^+(\text{solvated}) + cis\text{-TAA}^-$$

$$\updownarrow \text{slow}$$

$$\text{M}^+,\ trans\text{-TAA}^- \underset{\text{ion pair}}{\overset{\text{fast}}{\rightleftharpoons}} \text{M}^+(\text{solvated}) + trans\text{-TAA}^-$$

Each geometrical isomer of TAA⁻ gives rise to only one set of pmr signals, because ligand substitution involving the M⁺ ion pairs is undoubtedly very rapid. As the methyl proton signals at 2.19 and 2.05 ppm occur in a very concentrated DMSO-d_6 solution of NaTAA, they are assigned to methyl groups near the carbon–sulfur and carbon–oxygen bonds, respectively, of the cis isomer, which would be expected to be strongly ion-paired to Na⁺ in a bidentate chelate structure. In fact, these peaks markedly resemble in their positions and relative intensities the two methyl proton signals exhibited by M(TAA)₂ complexes. The peaks at 2.53 and 1.83 ppm, which increase in relative intensity as the

NaTAA concentration in DMSO-d_6 is decreased, are attributed to methyl groups near carbon–sulfur and carbon–oxygen bonds, respectively, in the trans isomer. Very little ion pairing would occur involving this isomer. The γ-proton signal to high field is assigned to the cis isomer, whereas the corresponding low field signal, which remains in dilute solutions, is attributed to essentially uncomplexed *trans*-TAA. Both the conductance and pmr data show that at a given concentration in DMSO solution dissociation is greater for the potassium salt than for the sodium salt.

The pmr spectra for four different 0.2 M NaTAA solutions are compared in Figure 6. The positions and intensities of the proton signals in deuterium oxide and methanol solutions exhibit the same type of concentration dependence as that observed in DMSO-d_6 solutions (Table VIII) and analogous assignments are suggested. In pyridine, only the methyl and vinyl proton peaks attributable to uncomplexed TAA⁻ are observed in 0.2–0.05 M NaTAA solutions.

Single-Crystal Structure and 5.0°K Polarized Electronic Spectra of Bis(monothioacetylacetonato)nickel(II). Far-Infrared and Raman Spectra of Bis(monothioacetylacetonato)metal(II) Complexes

Olavi Siiman, Donald D. Titus, Charles D. Cowman, James Fresco, and Harry B. Gray*

Contribution No. 4798 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, and the Department of Chemistry, McGill University, Montreal 110, Quebec, Canada. Received July 19, 1973

Abstract: A single-crystal X-ray structure of bis(monothioacetylacetonato)nickel(II) has been completed. The crystals are orthorhombic, space group P_{bca}, with eight molecules per unit cell: $a = 13.301$ (3), $b = 16.418$ (3), $c = 11.468$ (3) Å; $V = 2505$ (1) Å^3; $\rho_o = 1.52$ (2) and $\rho_c = 1.533$ g/cm^3. Diffractometer data were collected using Cu Kα radiation, and the structure was refined by full-matrix least-squares methods with anisotropic thermal parameters for all but the hydrogen atoms to a final $R = 0.072$ for 1676 independent reflections. The molecule is very nearly planar with a cis configuration of sulfur atoms about the nickel atom. Far-infrared and Raman spectra of Ni(II), Pd(II), Zn(II), and Cd(II) bis(monothioacetylacetonates) were recorded between 700 and 100 cm⁻¹. Normal coordinate analyses for the Ni(II) and Pd(II) complexes were made, assuming a C_{2v} 1 : 2 metal–ligand model. Bands attributable to M–S stretching vibrations occur at 251 and 194 cm⁻¹ in Ni(TAA)₂, 224 and 173 cm⁻¹ in Pd(TAA)₂, 273 and 197 cm⁻¹ in Zn(TAA)₂, and 245 and 180 cm⁻¹ in Cd(TAA)₂. The polarized single crystal absorption spectra of Ni(TAA)₂ at 5.0°K have been measured between 750 and 400 nm. The low intensity band at 630 nm is slightly π polarized, and is assigned $^1A_1 \rightarrow {}^1B_1$ ($d_{zz} \rightarrow d_{xy}$). Moderately intense features in the 500–400 nm region are assigned to d $\rightarrow$ b₁π^* and d $\rightarrow$ a₂π^* charge transfer transitions, based on the observed polarizations.

A wide variety of metal complexes of monothio-β-diketonates have been synthesized recently.[1] As cis and trans isomers are possible for both bis-planar and tris-octahedral metal monothio-β-diketonates, structural data are essential for any detailed interpretation of vibrational and electronic spectra. An early report[2] on bis(monothio-β-diketonates) alluded solely to a trans-planar configuration; however, X-ray investigation[3] of bis(monothiodibenzoylmethanato)palladium(II) revealed a cis planar arrangement about palladium. Further, pmr evidence[4] has indicated that tris(mono-thio-β-diketonato)cobalt(III) and -vanadium(III) exist exclusively as the cis (facial) isomers.

We have carried out an extensive investigation of the structural and spectroscopic properties of several bis(monothioacetylacetonato)metal(II) complexes, hereafter denoted M(TAA)₂, in an effort to provide a foundation for electronic structural discussion. In this paper we report complete X-ray crystallographic results and polarized single-crystal electronic spectra at 5°K for Ni(TAA)₂, as well as detailed analyses of the vibrational spectra of the (TAA)₂ complexes of Zn(II), Cd(II), Ni(II), and Pd(II).

Experimental Section

The preparation of Zn(TAA)₂, Cd(TAA)₂, Ni(TAA)₂, and Pd-

* Address correspondence to this author at the California Institute of Technology.

(1) (a) H. Cox and J. Darken, *Coord. Chem. Rev.*, 7, 29 (1971); (b) S. E. Livingstone, *ibid.*, 7, 59 (1971).

(2) S. H. H. Chaston and S. E. Livingstone, *Aust. J. Chem.*, 20, 1079 (1967).

(3) E. A. Shugam, L. M. Shkol'nikova, and S. E. Livingstone, *Zh. Strukt. Khim.*, 8, 550 (1967).

(4) R. H. Holm, D. H. Gerlach, J. G. Gordon, and M. C. McNamee, *J. Amer. Chem. Soc.*, 90, 4184 (1968).